

ALCOHOL REACTION KINETICS ON COPPER/ZINC OXIDE SURFACE

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ABSTRACT

Recent commercial and academic interest in CH_3OH synthesis via CO hydrogenation, together with the high selectivity and relative simplicity of this reaction, make it an ideal reaction for testing and comparing adsorption studies, proposed mechanisms, and macroscopic rate behavior for oxide-based catalysts. Adsorption studies of H_2 , H_2O , and CH_3OH on ZnO powders and model thin films of Cu/ZnO have resolved several discrete adsorption sites. Infrared and temperature programmed decomposition studies of adsorbed CH_3OH are used to determine the energetics of the $\text{CH}_3\text{O}_{(a)}$ and $\text{HCOO}_{(a)}$ decomposition steps at these sites. Comparative studies using model Cu/ZnO thin films have resolved features common to bulk ZnO and bulk Cu, as well as differences in behavior which can be attributed to the availability of ZnO lattice anions at the perimeter of the Cu clusters. The results suggest that Type I sites on ZnO do not have a major role in the CH_3OH synthesis reaction on Cu/ZnO catalysts. Instead, the CH_3OH reaction may occur preferentially at perimeter sites of Cu clusters.

INTRODUCTION

The reactivity of carbon-oxygen bonds in adsorbed oxygenated hydrocarbon intermediates is of fundamental importance in understanding the rates and selectivity of alcohol reactions on heterogeneous catalysts. Reactions of commercial interest include methanol synthesis, the direct synthesis of higher alcohols, alcohol decomposition (e.g., reforming, partial oxidation), etherification (e.g., production of MTBE as a gasoline blending agent), condensation (e.g., conversion to C-8 compounds on zeolites or other acid catalysts), and functionalization (e.g., amination reactions).

Work in our laboratory has focussed on understanding the surface reactions involved in the catalytic formation and decomposition of the simplest alcohol, CH_3OH . In particular, we have undertaken a systematic study of a series of model ZnO or Cu/ZnO catalyst surfaces using a combination of infrared spectroscopy, temperature programmed desorption and decomposition of adsorbates, and reactor measurements of transient and/or steady state kinetics. These studies are aimed at identifying the composition and geometry of various adsorption sites on the Cu/ZnO surface, the mechanism and kinetics of adsorbate reactions at the sites, and the importance of each site in the overall CH_3OH synthesis reaction.

In the present paper we describe selected results from our overall program. These results are chosen to illustrate two points: The importance of the formate intermediate in alcohol reactions on oxide surfaces and its role in maintaining hydrogenation selectivity, and the relative importance of adsorption sites on the

ZnO and Cu components of the catalyst surface.

EXPERIMENTAL

Comparative studies of high surface area powders and planar thin-film samples are performed in two independent apparatus. Studies of powder samples were performed in the IR-TPD cell shown in Fig. 1. The sample containing 50-100 mg of ZnO is deposited from an aqueous slurry onto the front face of the cell mirror, a silver disk which is soldered to the re-entrant inner wall of the cell body. The mirror disk can be heated using the attached cartridge heater, or cooled to 100 K by flowing cooled N₂ through the attached coolant tube. After sealing the front of the cell using a flange-mounted CaF₂ window, the cell is attached to a stainless steel gas handling system and positioned in the sample compartment of the FTIR spectrometer (Nicolet 604SX). Spectra are obtained in a two-pass transmission mode by reflecting the IR beam from the mirror disk, thereby passing through the sample layer twice. During a typical *in-situ* TPD experiment, IR spectra are recorded at regular temperature intervals (75 scans/spectrum, at a scan rate of 1-2 scans/sec; resolution = 8 cm⁻¹), while the flux of each desorbing species is monitored using a quadrupole mass spectrometer (Spectramass 800) attached to the gas handling system. All of the TPD experiments described here were performed with the IR-TPD cell evacuated and pumped by the gas handling system (i.e., no carrier gas is used).

The majority of the results described below were obtained using Kadox 25 ZnO, in order to examine the possible importance of the unique Type I adsorption sites for H₂ that have been reported for this material. The pretreatment required to activate the Type I sites involves (step 1) heating the sample in vacuum ($P < 10^{-6}$ torr) at 673 K for 3 hours, (step 2) cooling to 573 K and admitting 0.5 torr O₂ for 10 minutes, then evacuating (O₂ cycle repeated three times), and (step 3) re-heating in vacuum to 673 K for 20 minutes before cooling to room temperature.

Once the pretreatment steps were finished, the IR-TPD experiments for the adsorbate of interest could be repeated indefinitely. For experiments using CH₃OH and H₂O, both of which are irreversibly adsorbed at 300 K, a volumetrically determined amount of either gas is admitted from the gas handling system into the sample cell. For H₂ adsorption experiments, it is necessary to fill the sample cell with 40 torr H₂ at 300 K to occupy the Type I sites, since the Type I H₂ adsorption state desorbs readily at room temperature.

The complementary experiments using planar samples were performed in the apparatus shown schematically in Fig. 2. The sample configuration is shown schematically in the inset of the figure. Samples are prepared by first depositing thin films of ZnO onto Au substrates, using a separate RF plasma sputtering system (perkin Elmer model 2400) with a ZnO target and a background gas of 24% O₂ : 76% Ar at a pressure of 1 Pa. The ZnO deposition rate was 200 Å/min and the deposited film thickness was approximately 1 μm. X-ray diffraction measurements confirm that the film grains are preferentially oriented with their c-axis within 5° of the surface normal. Thus the films expose a high-fraction of (0001)-Zn planes and/or vicinal defect surfaces.

After the ZnO film has been deposited, a chromel-alumel thermocouple is attached to the Au substrate and the sample is mounted into the TPD apparatus shown in the main part of Fig. 2. The apparatus consists of an ion-pumped stainless-steel bell jar equipped with a single pass cylindrical mirror analyzer, a quadrupole mass spectrometer, an ion sputtering gun, a side chamber which contains a Cu evaporation source and a quartz film thickness monitor. The sample itself is mounted on a differentially pumped sliding seal transfer rod that

permits the sample to be translated between the evaporation chamber and the focal point of the CMA.

Two sequences are used to prepare surfaces with different Cu loadings. In most cases, the loading was controlled by changing the exposure time of a sputter cleaned ZnO surface to the Cu evaporant flux. The deposition flux was approximately $\text{\AA}/\text{min}$, as measured using the film thickness monitor. The sample temperature during evaporation is 300 K. An independent measure of the Cu coverage is obtained using Auger analysis to examine the surface after evaporation. For a few experiments, an alternate procedure for varying the Cu loading consists of initially evaporating a high coverage of Cu and then heating the sample progressively higher temperatures above 800 K to desorb increasing amounts of the initial Cu layer.

After recording the Auger spectrum of the surface following Cu evaporation, methanol decomposition experiments were performed by exposing the sample to CH_3OH at 300 K by backfilling the chamber. After the background pressure returned to ca. 10^{-10} torr, the sample is heated and the evolved products are monitored using the mass spectrometer. The heating rate used for the thin film experiments is 25 K/sec. Care is taken to stop each TPD experiment at a low enough temperature (ca 750 K) to prevent any loss of Cu by re-evaporation. Spectra for each of the observed products are usually recorded separately in repetitive experiments. Reproducibility between experiments is confirmed periodically by using multiplexed signal acquisition, at a cost in signal resolution. Reproducibility can also be confirmed by comparing the record of total pressure vs. time measured by the ionization gauge in the main chamber.

RESULTS

Porous sample studies: Role of Type I sites. In Fig. 3 we show the IR spectra acquired during the adsorption and subsequent TPD of CH_3OH on Type I activated ZnO. The bottom curve is the spectrum of the sample in the presence of 40 torr H_2 at 300 K, obtained prior to absorbing CH_3OH . The sharp band at 1709 cm^{-1} and the less intense band at 3491 cm^{-1} correspond to the Zn-H and O-H stretching vibrations, respectively, which are characteristic of H_2 adsorbed at Type I sites. We note that the band observed at 3618 cm^{-1} is attributed to a residual surface $\text{OH}_{(s)}$ species and is not associated with Type I H_2 adsorption. Features in the 2900 to 2800 cm^{-1} region are due to residual surface hydrocarbon impurities still remaining after the three 573 K O_2 cleaning cycles of the pretreatment. The concentration of Type I sites in this sample is $5.8\text{ }\mu\text{mole H}_2/\text{gm ZnO}$, as determined from the integrated area under an H_2 TPD spectrum.

The next curve is the spectrum obtained after evacuating the H_2 and adsorbing an amount of CH_3OH corresponding to $10\text{ }\mu\text{mole/gm}$. The bands appearing at 2932 and 2816 cm^{-1} are assigned to the asymmetric and symmetric C-H stretching vibrations of the surface methoxy species. We note that the adsorption of CH_3OH produces no new resolvable OH features in the region above 3500 cm^{-1} , nor does it perturb the residual surface OH band at 3618 cm^{-1} . If 40 torr of H_2 is admitted to the cell at this point, the Zn-H and O-H bands characteristic of Type I sites do not appear. This confirms that CH_3OH adsorbs irreversibly at Type I sites, blocking them from further H_2 adsorption. The fact that $10\text{ }\mu\text{mole CH}_3\text{OH/gm ZnO}$ are required to clock the sites completely indicates that some of the CH_3OH must be adsorbed at non-Type I sites, as well.

The next curve in Fig. 3 is the spectrum of the sample obtained at 530 K during the decomposition of the adsorbed CH_3OH . The intensity of the methoxy C-H bands at 2932 and 2816 cm^{-1} decreases, and new features grow in at 2875 , 1574 , 1364 , 1377 cm^{-1} . These new bands are assigned respectively to the C-H stretching

mode, the asymmetric and symmetric O-C-O stretching modes, and the in-plane C-H bending mode of a surface $\text{HCOO}_{(a)}$ species. The asymmetric O-C-O stretching mode and the in-plane C-H bending mode also produce an additional combination band at 2965 cm^{-1} . These results demonstrate the sequential conversion of $\text{CH}_3\text{O}_{(a)}$ species to $\text{HCOO}_{(a)}$ species.

A separate experiment was performed by interrupting the decomposition at 530 K (corresponding to the temperature at which the maximum $\text{HCOO}_{(a)}$ coverage is observed) and quickly cooling the sample to 300 K to preserve the surface $\text{HCOO}_{(a)}$ coverage. Admitting 40 torr of H_2 to the cell at this stage failed to produce IR bands at 3490 or 1710 cm^{-1} , thus indicating that the $\text{HCOO}_{(a)}$ species also block the Type I H_2 sites.

The uppermost curve is the spectrum of the sample obtained after completing the TPD experiment, cooling from 673 K to 300 K, adding 0.1 torr O_2 to improve the IR transmission, and then admitting 40 torr of H_2 . The bands at 3492 and 1709 cm^{-1} have now been restored, indicating that the Type I sites have been made vacant following decomposition of the adsorbed CH_3OH .

The product desorption spectra recorded by the mass spectrometer during the preceding experiment are shown in Fig. 4. The H_2 evolution curve has three resolvable features: a low temperature shoulder at 459 K, a broader shoulder near 511 K, and a desorption maximum at 565 K. The H_2 desorption at 565 K is accompanied by the almost coincident desorption of CO and CO_2 at 573 K. In contrast, the H_2 evolved at 459 K and 511 K is not accompanied by any significant amount of carbon oxides. This is a clear indication that the H_2 evolution peaks at 459 K and 511 K are a result of the conversion of $\text{CH}_3\text{O}_{(a)}$, while the nearly simultaneous desorption of H_2 , CO , and CO_2 at 565-573 K is due to the decomposition of the surface $\text{HCOO}_{(a)}$. Figure 4 also shows that H_2O is not a favored product of either $\text{CH}_3\text{O}_{(a)}$ conversion or $\text{HCOO}_{(a)}$ decomposition, despite the oxidized condition of the ZnO sample.

To determine the importance of Type I sites on ZnO for CH_3OH decomposition, we next performed a series of experiments using pre-adsorbed H_2O to block the Type I sites before adsorbing CH_3OH . Infrared spectra recorded in the presence of 40 torr of H_2 before and after H_2O was admitted to the cell showed that H_2O also adsorbs irreversibly into the Type I H_2 sites, blocking them from H_2 adsorption. Methanol was then admitted to the sample with the blocked Type I sites. Adsorption still occurs, as indicated by the IR spectrum which showed the C-H vibrational bands of the $\text{CH}_3\text{O}_{(a)}$ intermediate. The fact that CH_3OH dissociatively adsorbed even on the Type I blocked sample confirms that CH_3OH adsorbs at non-Type I sites.

The TPD product desorption spectra recorded for the sample with co-adsorbed H_2O and CH_3OH are shown in Fig. 5. The first feature to note is the behavior of the H_2O desorption signal. A small amount of desorption is observed near 475 K; however, the majority of the H_2O desorbs with a peak maximum near 600 K. This is identical to the desorption behavior of pure H_2O (i.e., without co-adsorbed CH_3OH). This indicates that the H_2O molecules adsorbed in Type I sites retain their identity throughout the experiment, that the Type I sites remain blocked by H_2O throughout the temperature range of CH_3OH decomposition, and that the adsorbed H_2O is not consumed in the formation of CO_2 during the formate decomposition step.

A small amount of molecular CH_3OH desorbs between 400 K and 500 K. A similar molecular CH_3OH desorption peak can be observed from samples containing no pre-adsorbed H_2O , provided the initial CH_3OH coverage is greater than 10 $\mu\text{mole/gm}$. This indicates that there is a finite combined concentration of both Type I and non-Type I sites at which CH_3OH is dissociatively adsorbed. Additional CH_3OH beyond this amount is adsorbed into a less tightly bound state

which desorbs molecularly at 450 K. The low temperature shoulder in the H₂O desorption spectrum probably arises from a similar state.

Dissociatively adsorbed CH₃OH ultimately decomposes to yield H₂, CO, and CO₂. The H₂ evolution curve shows two resolved maxima at 493 K and 557 K, corresponding to the two highest temperature features in the H₂ desorption spectrum for decomposition of CH₃OH alone (cf. Fig. 4). However, the desorption shoulder at 459 K that was observed on the H₂O-free surface is absent! In addition, the H₂ desorption maximum at 493 K occurs without evolution of carbon oxides, while the H₂ maximum at 557 K is followed by the evolution of CO and CO₂ at 567 K and 581 K, respectively. Since the only difference between the experiments shown in Figs. 4 and 5 is the presence of pre-adsorbed H₂O in the Type I sites, we conclude that the H₂ peak at 493 K corresponds to the decomposition of surface methoxy species adsorbed at non-Type I sites, while the H₂ desorption feature observed at 459 K (on the H₂O-free surface) can be assigned to the decomposition of methoxy species adsorbed at Type I sites.

The decomposition of the remaining surface formate species gives rise to the H₂, CO, and CO₂ peaks between 557 and 581 K. The spread in temperature between the three species appears to be real, and may result from re-adsorption effects for CO and CO₂ which are more pronounced on samples with pre-adsorbed H₂O due to a short-lived re-generation of transient HCOO_(a) species involving the adsorbed H₂O molecules. However, the desorption temperatures are similar to those observed in the absence of pre-adsorbed H₂O, indicating that the decomposition rate of the formate species is insensitive to Type I vs. non-Type I sites.

However, the CO₂:CO ratio is much greater than in the absence of pre-adsorbed H₂O. As noted above, this is not because pre-adsorbed H₂O at the Type I sites is incorporated into the CO₂ product. Instead, it appears that the decrease in CO intensity is a direct result of the blockage of Type I sites by H₂O. Thus we conclude that formate species produced at Type I sites decompose selectively to CO, while formate species at non-Type I sites decompose selectively to CO₂.

Thin film studies: Role of Cu sites. The product distribution resulting from CH₃OH decomposition on a clean, (0001) oriented ZnO thin film is shown in Fig. 6. The initial CH₃OH exposure is 5 L for each experiment (1 Langmuir = 10⁻⁶ torr sec). The observed product include H₂, CH₂O, CO, and CO₂. We also looked for but did not observe desorption peaks for CH₄ and H₂.

Consistent with the results for ZnO powder described above, the spectra show that adsorbed CH₃OH decomposes in two well-resolved processes. The 585 K process corresponds to decomposition of the CH₃O_(a) intermediate, and is characterized by the evolution of H₂ without CO or CO₂. The 585 K process also produces a small amount (ca. 20%) of desorbed CH₂O. The balance of the CH₂O is apparently stabilized immediately, being converted to a formate precursor before it is able to desorb.

The 635 K process corresponds to the decomposition of HCOO_(a) to produce H₂, CO, and a small amount of CO₂. Some additional CH₂O is also observed at 635 K, which may result either from the delayed decomposition of a limited number of CH₃O_(a) species whose decomposition had been sterically impeded by occupied neighboring sites until 635 K. Alternatively, the CH₂O signal at 635 K may also result from the hydrogenation of a limited number of HCOO_(a) species, using the H_(a) atoms released by the decomposition of the remaining HCOO_(a) species.

The apparent activation energies of the 585 K and 635 K processes are 35 and 38 kcal/mole, respectively, based on the Redhead equation for first-order decomposition kinetics and an assumed pre-exponential factor of 10¹³ sec⁻¹. These values are comparable to the activation energies for the CH₃O_(a) and

HCOO_(a) decomposition steps computed for the powder experiments, i.e., 31 and 33 kcal/mole for the CH₃O_(a) decomposition on Type I and non-Type I sites, respectively, and 40 kcal/mole for HCOO_(a) decomposition. Comparison of the energies for CH₃O_(a) decomposition on Type I vs. non-Type I sites suggests that Type I sites may in fact be absent from the Ar⁺ ion sputtered and annealed ZnO thin film surfaces. We also note that the observation of CH₂O during the experiments on thin film ZnO samples is a result of the line-of-sight detection provided by the mass spectrometer when using a planar sample. Formaldehyde may also be produced initially during CH₃O_(a) decomposition on powdered ZnO, but may not be detectable due to irreversible re-adsorption on the pore walls before it can diffuse out of the powdered sample.

Figure 7 shows the product desorption spectra for CH₃OH decomposition on an evaporated Cu/ZnO sample. The Cu loading in this case is sufficient to decrease the Zn Auger signal to 35% of its clean-surface value. The CH₂O, H₂, CO, and CO₂ desorption features at 585 K and 635 K are still present, but are significantly attenuated. This indicates that CH₃OH decomposition is still occurring on ZnO sites, which implies that even at this high Cu loading, the Cu layer does not cover the ZnO surface uniformly.

Two differences from the decomposition behavior of clean ZnO are also observed. First, small H₂ and CH₂O desorption signals are observed near 410 K, and a small CO₂ peak is observed near 510 K. These features are quite similar to the CH₃OH decomposition behavior reported for metallic Cu⁽¹⁾. This suggests that at least a portion of the evaporated Cu layer has agglomerated to form metallic Cu clusters, which are large enough to demonstrate the same CH₃OH decomposition behavior as bulk Cu.

The second difference is the large CO₂:CO ratio observed for the 635 K process. This is reminiscent of the HCOO_(a) decomposition selectivity observed when H₂O was pre-adsorbed on powdered ZnO, and suggests that a portion of the evaporated Cu layer is sufficiently highly dispersed to perturb the decomposition selectivity of the HCOO_(a) species on the ZnO surface. We cannot suggest a mechanism for this perturbation at this time.

As the final experiment described here, we sought to test the influence of surface oxidation state on the CH₃OH decomposition behavior of the evaporated Cu/ZnO thin film sample. Figure 8 shows the product desorption spectra for the same Cu/ZnO sample described above, following sequential exposure to 2 L of O₂ and 5 L of CH₃OH. Three main features are noted:

- The CO and CO₂ peaks at 635 K are unchanged from their intensities in the O₂-free case. However, the H₂ and CH₂O signals in the region of the 585 and 635 K decomposition processes have been essentially eliminated. Since pre-exposure to O₂ had no effect on the CH₃OH decomposition behavior of a clean ZnO thin film, this suggests that the dispersed Cu species proposed above also influence the O₂ adsorption character of the ZnO surface.

- The H₂ peak at 410 K is enhanced by a factor of two, relative to the case without pre-adsorbed O₂. The CH₂O peak at 410 K is also somewhat enhanced. This is consistent with earlier workers' results that pre-exposure to O₂ enhances the reactive sticking coefficient of CH₃OH on Cu surfaces, and indicates that this enhancement also occurs on the small Cu clusters present on the Cu/ZnO thin film studied here.

- The CO₂ peak at 510 K is greatly enhanced following O₂ pre-exposure. This result is also consistent with the behavior of metallic Cu, where adsorbed O_(a) is expected not only to enhance dissociative CH₃OH adsorption but also to increase the conversion of CH₃O_(a) to stable HCOO_(a), which in turn is reported to decompose almost exclusively to CO₂.

Similar results to those described above were obtained for a series of Cu

loadings on ZnO thin films. In general, the low temperature decomposition processes at 410 K and 510 K were observed at every Cu loading. Interestingly, the enhancement effect of pre-adsorbed O_2 was observed only for higher Cu loadings. This it appears that metallic Cu clusters at the lowest loadings are small enough to activate dissociative CH_3OH adsorption without pre-adsorbed $O(a)$. This may be the result of a spillover effect of dissociated $H(a)$ atoms onto the ZnO support. For large clusters, the influence of the spillover effect would be limited to Cu atoms near the perimeter of the cluster, and the $O(a)$ enhancement would be necessary to activate the remaining atoms in the cluster.

One other result is the fact that the method for preparing different Cu loadings had no effect on the CH_3OH decomposition behavior; i.e., samples prepared by progressive evaporation of increasing amounts of Cu behaved identically with samples prepared by successive heating of a high initial Cu loading to leave behind progressively decreasing amounts of Cu. We interpret this to indicate that both the cluster and dispersed Cu species are present in a thermodynamically equilibrated state.

DISCUSSION

Role of formate intermediates. The present results largely confirm our previous understanding that CH_3OH decomposition to CO or CO_2 occurs via the $CH_3O(a)$ and $HCOO(a)$ intermediates. For the powdered ZnO, we have shown that the selectivity of the $HCOO(a)$ decomposition processes is sensitive to the geometry of the adsorption site: Type I sites yield CO as the major product, while non-Type I sites, possibly as a result of the presence of co-adsorbed H_2O , yield primarily CO_2 . The effect of the dispersed Cu species on the Cu/ZnO thin film samples is also to increase the selectivity for $HCOO(a)$ decomposition toward the CO_2 product. The latter result, of course, may also be due to a chemical effect, but it does serve to illustrate the role of the composition of the active site on the selectivity of elementary desorption or decomposition steps.

Our results using clean ZnO thin films also suggest for the first time the possibility that the $HCOO(a)$ intermediate on the oxide surface may be hydrogenated to produce CH_2O (cf., the CH_2O desorption peak at 635 K in Fig. 6). Additional work is needed to eliminate the alternate explanation (i.e., the delayed decomposition of $CH_3O(a)$ species due to neighboring site blockage), but together with the observation that CH_2O does not reach the mass spectrometer in the powdered ZnO experiments due to readsorption, this raises the possibility that the CH_3OH synthesis mechanism may involve discrete CO and CH_2O hydrogenation steps, with gas phase CH_2O as a short-lived intermediate present at low concentrations.

Role of Type I sites vs. Cu. The IR spectra in Fig. 3 clearly demonstrate that CH_3OH adsorbs dissociatively at Type I sites. The site blocking experiments using pre-adsorbed H_2O show equally clearly that CH_3OH is also adsorbed in non-Type I sites. The subsequent TPD experiments show that $CH_3O(a)$ species adsorbed at Type I vs. non-Type I sites behave differently. The $CH_3O(a)$ decomposition step occurs 35 K earlier (ca. 2 kcal/mole lower apparent activation energy) at Type I sites, and the resulting $HCOO(a)$ intermediate subsequently decomposes to yield primarily CO, with an apparent activation energy of 40 kcal/mole.

However, it is also important to recognize the converse of this observation, namely that $CH_3O(a)$ species adsorbed in non-Type I sites also decompose cleanly to yield the $HCOO(a)$ intermediate, with an apparent activation energy only 2

kcal/mole greater than for Type I sites. Moreover, evolution of H_2 (as opposed to H_2O) is also observed for the $CH_3O(a)$ decomposition step at non-Type I sites. Since the Type I sites remain blocked by H_2O throughout the $CH_3O(a)$ and $HCOO(a)$ decomposition processes, this indicates that Type I sites are not essential for either CH_3OH decomposition or molecular H_2 desorption from ZnO surfaces.

The origin of the modest enhancement of the $CH_3O(a)$ decomposition kinetics at the Type I sites may be attributed to the enhanced basicity of the O^- anion of the Type I site. A variety of spectroscopic evidence exists to indicate that the Type I sites are located at cation vacancies on the (0001)-Zn polar surface of $ZnO^{(2)}$. The electrostatic potential at these cation vacancies can be expected to induce a larger proton affinity in the neighboring O^- anions.

Ironically, our hard-won understanding of the behavior of Type I sites now leads us to seriously question the importance of these sites as active participants in the CH_3OH synthesis reaction on Cu/ZnO catalysts. In no case did we observe CH_3OH desorption from $CH_3O(a)$ species adsorbed in Type I sites. We did observe the analogous desorption process for H_2O adsorbed at these sites, but with a desorption energy of 40 kcal/mole, significantly greater than the activation energy for $CH_3O(a)$ decomposition. This large activation energy for recombinative desorption of molecules containing OH groups is also a reflection of the basicity of the Type I O^- anion, and suggests that CH_3OH desorption from Type I sites would be more difficult than from non-Type I sites.

Secondly, the modest enhancement for the $CH_3O(a)$ decomposition step at Type I sites is small, relative to the enhancement for both the $CH_3O(a)$ and $HCOO(a)$ decomposition steps observed when Cu was evaporated onto the ZnO surface. While it does not necessarily follow that the activation energy for the reverse $CH_3O(a)$ synthesis reaction is also reduced as dramatically, this observation does suggest that the presence of the Cu component will have a more significant influence than the presence of the geometrically distinct Type I sites.

Finally, the large binding energy observed for H_2O in Type I sites suggests that these sites may be blocked under CH_3OH synthesis conditions, since the reactant mixture usually contains added CO_2 that would be converted to H_2O via the reverse shift reaction.

Thus the present results strongly suggest that the origin of the CH_3OH synthesis activity in the Cu/ZnO catalyst does not reside in the Type I sites found on ZnO. This does not rule out the possibility that analogous sites may be present at isolated Cu cations on the surface of Cu/ZnO catalysts; evidence for the influence of a dispersed Cu species is seen in the Cu/ZnO thin film experiments shown in Figs. 7 and 8. However, the Cu/ZnO experiment also indicate that the $CH_3O(a)$ decomposition activity of the metallic Cu clusters is much greater than for either Type I or non-Type I sites. Moreover, the ZnO support provides a spillover effect which enhances the CH_3OH decomposition activity of the Cu clusters even more, by eliminating the need for pre-exposure to O_2 to provide proton acceptor sites.

ACKNOWLEDGEMENT

This work has been supported by the National Science Foundation, through grant Nos. CPE-8110754 and RI0-CPE-8105823. One of us (D. L. R.) acknowledges stipend support from Chevron Research Company, Standard Oil of California.

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TPD Cell for Transmission-Reflectance Infrared Spectroscopy

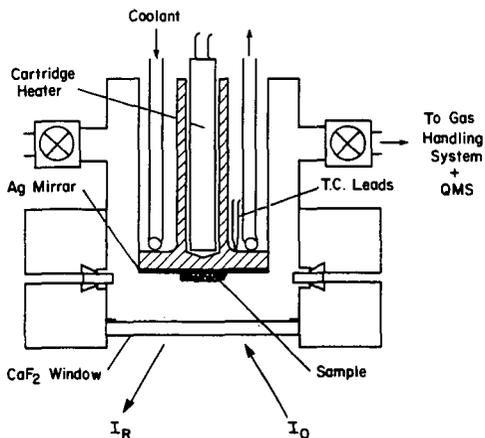


Figure 1. Schematic diagram of sample cell used for combined TPD and IR studies of catalyst powders.

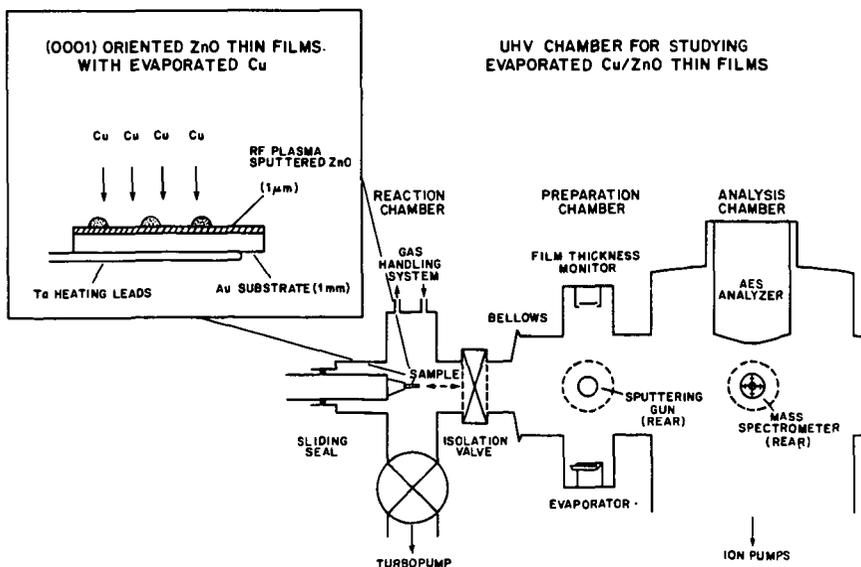


Figure 2. Apparatus used for TPD studies on Model Cu/ZnO thin films. Inset: Schematic representation of RF sputtered thin film sample configuration, with *in-situ* evaporate Cu overlayer.

IR SPECTRA DURING CH₃OH DECOMPOSITION
ON TYPE I ACTIVATED ZnO (Kadox 25)

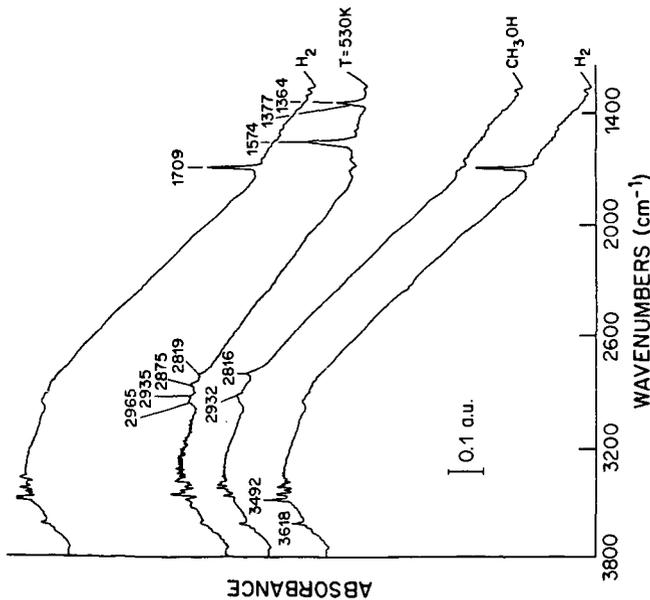


Figure 3. Infrared spectra of CH₃OH and H₂ adsorbed on Type I activated ZnO. Bottom curve is H₂ alone at 300 K. Second curve sample, cooled to 530 K, after CH₃OH adsorption. Top curve is CH₃OH alone at 300 K. Top: same sample after heating to 573 K, then exposed to 40 torr H₂ at 300 K.

PRODUCT DISTRIBUTION DURING CH₃OH
TPD ON ZnO (Kadox 25)

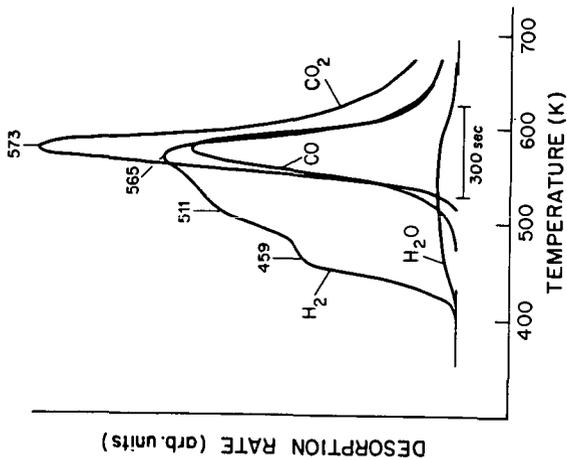


Figure 4. Product distribution spectra during TPD of CH₃OH adsorbed on Type I activated ZnO.

PRODUCT DISTRIBUTION DURING CH₃OH
TPD ON ZnO (Kodak 25):
INFLUENCE OF PRE-ADSORBED H₂O

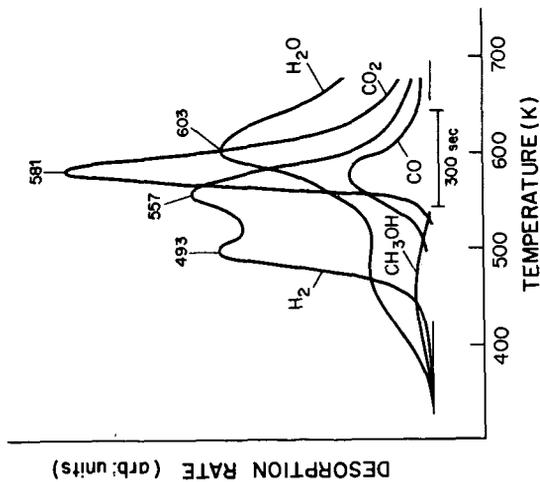


Figure 5. Product distribution spectra during TPD of co-adsorbed CH₃OH and H₂O on ZnO, where H₂O is adsorbed first to blank Type I sites.

TEMPERATURE PROGRAMMED DECOMPOSITION
OF CH₃OH ADSORBED ON Cu/ZnO(OOOO) FILMS

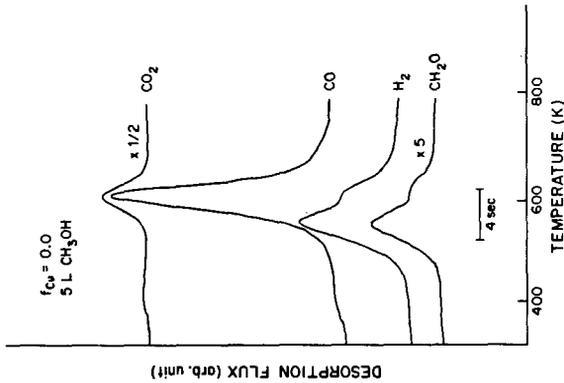


Figure 6. Product distribution spectra during TPD of CH₃OH adsorbed on clean, oriented ZnO thin films.

TEMPERATURE PROGRAMMED DECOMPOSITION
OF CH₃OH ADSORBED ON Cu/ZnO(0001) FILMS

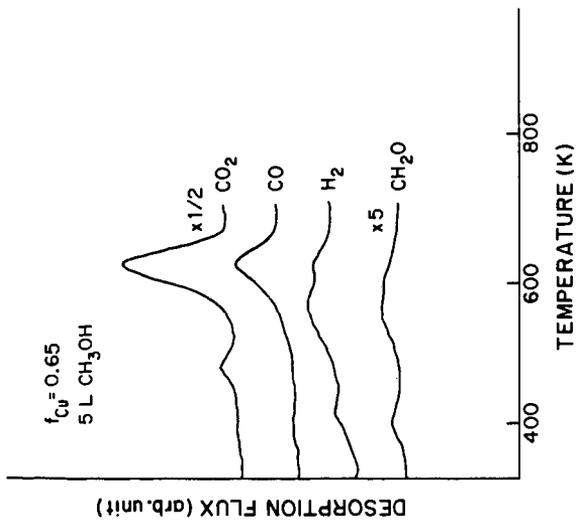


Figure 7. Product distribution spectra during TPD of CH₃OH adsorbed on a Cu/ZnO surface. (Auger intensity ratio $I_{Cu}/(I_{Cu} + I_{Zn}) = 0.65$).

TEMPERATURE PROGRAMMED DECOMPOSITION
OF CH₃OH ADSORBED ON Cu/ZnO(0001) FILMS:
INFLUENCE OF PRE-ADSORBED O₂

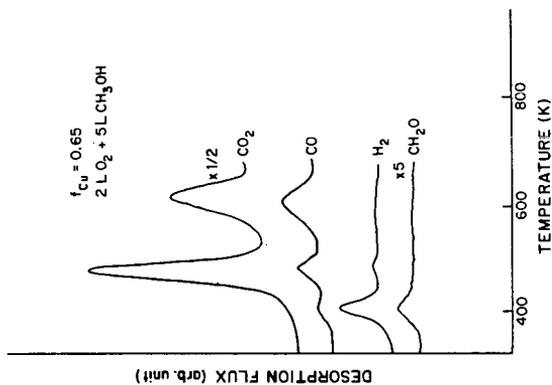


Figure 8. Product distribution spectra during TPD of CH₃OH on Cu/ZnO surface that has been pre-exposed to 2 L of O₂ before CH₃OH adsorption.

EFFECT OF OXIDATION STATES ON THE SYNGAS ACTIVITY OF
TRANSITION-METAL OXIDE CATALYSTS

By

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INTRODUCTION

Supported Rh catalysts and Rh-containing mixed oxide catalysts have been studied extensively (1-5) for Fischer-Tropsch activity and their ability to produce different distributions of oxygenated products. Ichikawa and co-workers (1, 2) correlated X-ray photoelectron spectroscopy (XPS) measurements on the electronic state(s) of supported Rh catalysts with their corresponding Fischer-Tropsch oxygenate distributions and concluded that for selective C_2 -oxygenate formation both Rh^0 and Rh^+ sites were required; the Rh^0 sites functioned as CO dissociation sites in the formation of alkyl groups, while Rh^+ served as the site for associative CO adsorption and subsequent CO insertion to form intermediate acyl species. Similarly, Wilson et al. (3) concluded that the stabilization of Rh^+ by Mn promoters in silica-supported Rh catalysts may be responsible for the enhanced C_2 -oxygenated selectivity under syngas reaction conditions.

Somorjai and co-workers (4, 5), using a different approach, studied the syngas activity of Rh_2O_3 and $LaRhO_3$ at different temperatures and presumably different levels of reduction and also concluded that for selective C_2 and C_2^+ oxygenate formation to occur efficiently, Rh^0 and Rh^+ are required for facile CO dissociation and CO insertion, respectively. Thus there are strong implications as to the importance of oxidation states of group 8 metals in controlling the linear oxygenate selectivity and product distribution. To better understand the relationship between transition-metal oxidation states and catalytic

performance, we synthesized high-purity LaRhO_3 and GdCoO_3 and characterized and evaluated these catalysts at different levels of reduction to determine the existence and thus the importance of different Rh and Co oxidation states. Where appropriate, comparisons are made with a conventional Rh/SiO_2 catalyst.

Cu-based, low-pressure CH_3OH synthesis catalysts represent another system in which oxidation states are important. Recent evidence suggests that Cu^+ species are the active components for CO activation in both Cu-ZnO (6) and Cu-Cr oxide (7, 8) catalysts. Others (9), however, have used XPS to examine the oxidation states of Cu in Cu-ZnO and report the existence of only Cu^0 species under reaction-like reducing conditions. Yet others (10) propose that both Cu^0 and Cu^+ are essential for selective CH_3OH formation, with Cu^+ providing sites for CO activation and Cu^0 the sites for dissociative H_2 chemisorption. We present data for alkali- and alkaline-earth-promoted Cu-Cr oxide that support the hypothesis that Cu^0 serves as the site for H_2 chemisorption and that both Cu^0 and Cu^+ sites are required for Cu-Cr oxide to efficiently catalyze the formation of CH_3OH from syngas.

RESULTS AND DISCUSSION

Characterization and Catalytic Activity of LaRhO_3 and GdCoO_3

We prepared GdCoO_3 by high-temperature calcination (650 °C) of the stoichiometric thermal precursor $\text{GdCo}(\text{CN})_6 \cdot n\text{H}_2\text{O}$, using the method outlined by Gallagher (11). We prepared LaRhO_3 in high purity by converting a mixture of La_2O_3 and Rh_2O_3 (5% excess of La_2O_3 over the 1:1 stoichiometry) to the nitrates, using HNO_3 , and then firing in air to 1000 °C for 24 h. The excess La_2O_3 was removed from LaRhO_3 by leaching with warm 20% acetic acid (12-14). Powder X-ray diffraction

measurements showed that both GdCoO_3 and LaRhO_3 were of high purity; no diffraction lines that could be attributed to the simple oxides were detected in either sample.

The temperature-programmed reduction (TPR) spectra of LaRhO_3 and GdCoO_3 (Figure 1) illustrate their stability with respect to reduction in flowing H_2 at 1 atm pressure. Under reaction conditions used in this study, 800 psig of $\text{H}_2/\text{CO} = 1/1$, the TPR peaks would be shifted to lower temperatures. We calculated the extent of the shift for the H_2O peaks of the GdCoO_3 sample, using the method described by Gentry et al. (15). Under reaction conditions, the H_2O peaks centered at 415 and 515 °C would be shifted to ~307 and 390 °C, respectively. A shift of about 100 °C under reaction conditions should be expected for LaRhO_3 too, giving an H_2O peak centered at ~300 °C.

Prior to catalytic evaluation, GdCoO_3 was subjected to various levels of prereduction by stopping the TPR experiment at different temperatures. The levels of reduction were determined from the number of H_2O molecules formed during reduction. These data are summarized in Table I; the sample corresponding to 30% reduction was prepared in a recirculation loop reactor maintained at 510 °C. Table I also gives the relevant reduction data for LaRhO_3 . Powder X-ray diffraction (XRD) measurements for the GdCoO_3 samples reduced to the 20% and 30% levels showed peaks for Co^0 and Gd_2O_3 only. The XRD pattern for the 10% reduced sample gave peaks corresponding to Gd_2O_3 (and by necessity Co^0 , since any cobalt oxide formed along with Gd_2O_3 would be reduced to Co^0), GdCoO_3 , and a phase tentatively identified as the defect-type perovskite, $\text{GdCo}_{0.92}\text{O}_{2.5}$.

The powder XRD of the LaRhO_3 sample after the TPR experiment gave only broad peaks for Rh^0 and La_2O_3 . This is important, since the TPR conditions are similar to those encountered under Fischer-Tropsch

reaction conditions. X-ray photoelectron spectra of LaRhO_3 after various in situ reduction pretreatments (Figure 2) show that only Rh^0

Table I. Temperature-Programmed Reduction Data for GdCoO_3 and LaRhO_3

	T_{max} ($^{\circ}\text{C}$)	$\#\text{O}^{2-}$ removed	% reduction ^a
$\text{GdCoO}_3^{\text{b}}$	510	7.1×10^{24}	30
	535	4.6×10^{20}	20
	490	3.0×10^{20}	13
	455	2.2×10^{20}	10
$\text{LaRhO}_3^{\text{c}}$	535	1.45×10^{20}	24

^aMaximum extent of reduction under these conditions is 50%, since both Gd_2O_3 and La_2O_3 are stable with respect to reduction at $T < 800^{\circ}\text{C}$. ^b350-mg sample contains $2.4 \times 10^{21} \text{O}^{2-}$. ^c100-mg sample contains $6.1 \times 10^{20} \text{O}^{2-}$.

is present on the surface after H_2 (1 atm pressure) reduction at 300°C . Reduction at 300°C in a 2:1 H_2/CO flow at 1 atm total pressure, however, stabilizes some of the LaRhO_3 from reduction to Rh^0 , as evidenced by the Rh^{3+} peak. Deconvolution of the Rh $3d_{5/2}$ portion of the XPS spectrum could be fitted into two Gaussian components attributable to Rh^{3+} and Rh^0 , with no Rh^+ component in the 308-eV region of the spectrum. These results differ from those of Somorjai under similar conditions, which may be due to the difference in purity of the starting LaRhO_3 samples. Repetition of the preparative technique outlined by Somorjai resulted in a residual Rh_2O_3 component

as detected by XPS, which was readily reduced to Rh^0 after H_2 reduction at 250 °C.

The Fischer-Tropsch activities for LaRhO_3 at different reaction temperatures are displayed as Schulz-Flory plots in Figure 3. At reaction temperatures ≥ 300 °C, the rates of C_2 -oxygenates ($\text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$) are greater than for CH_3OH , suggesting that the mechanism for CH_3OH formation is different from the mechanism for formation of higher oxygenates; the latter products apparently formed by CO insertion into surface alkyl fragments, as others (1, 16) have noted. Since XPS did not detect any Rh^+ on LaRhO_3 after a much milder pretreatment at 300 °C and the TPR curve showed that at 400 °C in 1 atm of H_2 , 50% of the lattice O^{2-} associated with Rh in LaRhO_3 had been removed, it is difficult to envision the existence of stable Rh^+ on the catalyst surface under our reaction conditions.

The Fischer-Tropsch results for reduced GdCoO_3 (Figure 4) corroborate those for LaRhO_3 and show that the most highly reduced samples form the highest proportion of C_2 and greater oxygenates. Again, it is difficult to envision the existence of partially oxidized, catalytically active Co species after those high levels of catalyst reduction.

These results suggest there is no need to invoke Rh^+ or lower-valent oxidation states of Co to explain the higher rates of C_2 -oxygenate formation. Rather, the poor CO dissociation capabilities of Rh^0 and Co^0 (17) require high temperatures and/or large metallic aggregates to efficiently dissociate CO and form surface alkyl fragments in high enough surface concentration, so that CO insertion into the metal-alkyl bond (to form acyl species) can compete favorably with hydrogenation of adsorbed CO and surface alkyls to form CH_3OH and paraffins, respectively.

This conclusion is supported by the results from a TPD/TPR sequence for CO adsorbed on a conventional 1.5% Rh/SiO₂ catalyst. The Fischer-Tropsch activity at 270 °C, 850 psig, and 2:1 H₂/CO gave 25% molar oxygenate selectivity and a C₂-oxygenate/CH₃OH ratio of 2.5. The TPD analysis in flowing He gave multiple CO desorption peaks with T_{max} values ranging from 70 to 257 °C, as well as a large CO₂ peak (from disproportionation of CO) centered at 300 °C. The TPR analysis in flowing H₂ immediately after the TPD experiment (no additional catalyst treatment) gave a large CH₄ peak centered at 219 °C. This series of experiments shows that high temperatures are required for CO dissociation to occur efficiently on supported Rh⁰ surfaces and that hydrogenation of the surface carbon to form CH₄ (or surface alkyls) occurs easily once the C-O bond is ruptured. The presence of CO desorption peaks at temperatures up to 257 °C also shows that associatively adsorbed CO is present under typical reaction conditions.

Characterization and Catalytic Activity of Promoted Cu-Cr Oxide

In earlier studies (7, 8), we showed that specific rates of CH₃OH formation were proportional to the amount of CuCrO₂ in the Cu-Cr oxide catalyst and the fraction of Cu⁺ present on the surface of the catalyst, which also contained Cu⁰. One may thus expect that high-purity CuCrO₂, which is stable under reaction conditions, would be most active. The data in Table II show that this is not the case and suggest that Cu⁰ is essential for the reduction of CO to form CH₃OH.

A series of alkali- and alkaline-earth-promoted Cu-Cr oxides (at the same molar loading) were prepared from the same batch of Cu-Cr oxide and evaluated for CH₃OH formation. The results and relevant kinetic information (Table III) show a strong promotional effect for

Table II. Effect of High-Temperature Calcination on Catalytic and Physical Properties of Cu-Cr Oxide

catalyst	surface area (m ² /g)	activity $\left(\frac{\mu\text{mol CH}_3\text{OH}}{\text{s}\cdot\text{m}^2 \text{catalyst}}\right)$	$\left(\frac{\text{Cu}^+}{\text{Cu}_{\text{tot}}}\right)^{\text{a}}$	composition ^b after T _{red} = 270 °C in H ₂
1/1 Cu/Cr (T _{calc} = 350 °C, for 2 h)	21.4	0.02	0.21	CuCrO ₂ (minor) Cu ⁰ (major)
1/1 Cu/Cr (T _{calc} = 1000 °C, for 4 h)	2.9	0.06	0.5	CuCrO ₂ (major) Cu ⁰ (major)
1/1 Cu/Cr (T _{calc} = 1000 °C, for 24 h)	0.3	≈ 0	1.0	CuCrO ₂ (only)

^aDetermined by XPS after H₂ reduction at 270 °C. ^bDetermined by powder X-ray diffraction.

CH₃OH formation and a lowering of the apparent activation energy for CH₃OH formation when a promoter is present.

The H₂ and CO chemisorption data in Table IV show that the enhanced catalytic activity is not due to an increase in CO adsorption (Cu⁺ sites). The TPD spectra of CO for unpromoted, Ba-promoted, and Cs-promoted Cu-Cr oxides are virtually identical in normalized intensities and position (T_{max}), supporting the conclusion that CO activation is not the source of the promoter effect; likewise, XPS measurements gave essentially identical surface fractions of Cu⁺ for these samples.

Table III. Rates of CH₃OH Formation and Kinetic Parameters for Promoted Cu-Cr Oxide Catalysts. Reaction Conditions: 270 °C, H₂/CO = 2/1, 800 psig pressure

catalyst	surface area (m ² /g)	rate ($\frac{\mu\text{mol}}{\text{g cat-s}}$)	rate ($\frac{\mu\text{mol}}{\text{m}^2 \text{ cat-s}}$)	E _{app} ($\frac{\text{kcal}}{\text{mol}}$)	reaction orders (H ₂) (CO)	
Cu-Cr oxide	69.2	0.61	0.009	19.4	0.56	0.57
(3.4% K) Cu-Cr oxide	--	9.30	--	--	--	--
(11.2% Cs) Cu-Cr oxide	75.0	9.83	0.13	13.4	--	--
(3.5% Ca) Cu-Cr oxide	--	3.74	--	--	--	--
(7.7% Sr) Cu-Cr oxide	--	9.04	--	--	--	--
(12% Ba) Cu-Cr oxide	56.8	14.54	0.26	10.9	0.56	0.62

The H₂ chemisorption data show that although the H₂ chemisorption values at the reaction temperature of 250 °C vary only slightly, the temperature dependencies for H₂ chemisorption are much lower for the promoted catalysts. This lower temperature dependency for H₂ chemisorption may be reflected in the lower E_{app} values for CH₃OH formation. The sites for H₂ chemisorption appear to be Cu⁰ centers, since there was no measurable H₂ uptake on ultrapure CuCrO₂ (no surface Cu⁰ detected by XPS) or Cr₂O₃ at 250 °C, yet H₂ chemisorption readily occurred at 250 °C on 99.99% Cu⁰ powder (Aldrich).

In addition, the levels of reduction of both the Ba- and Cs-promoted samples were ~1/3 that of the unpromoted sample, 12% vs. 37%, respectively, as determined by quantitative TPR and neutron activation analysis. Therefore, the comparable levels of H₂ chemisorption at 250 °C imply greater Cu⁰ particle dispersions for the promoted samples.

Table IV. H₂ and CO Chemisorption Data for Ba-Promoted, Cs-Promoted, and Unpromoted Cu-Cr Oxides

catalyst	(molecules/m ² catalyst)		
	T = 25 °C	T = 150 °C	T = 250 °C
Cu-Cr oxide (69.2 m ² /g)			
H ₂	1.8 x 10 ¹⁶	1.4 x 10 ¹⁷	6.2 x 10 ¹⁷
CO	6.0 x 10 ¹⁶	--	3.2 x 10 ¹⁷
(Ba) Cu-Cr oxide (56.8 m ² /g)			
H ₂	1.4 x 10 ¹⁷	3.9 x 10 ¹⁷	6.2 x 10 ¹⁷
CO	8.6 x 10 ¹⁶	--	5.1 x 10 ¹⁷
(Cs) Cu-Cr oxide (75 m ² /g)			
H ₂	1.3 x 10 ¹⁷	2.1 x 10 ¹⁷	2.6 x 10 ¹⁷
CO	1.2 x 10 ¹⁷	--	6.2 x 10 ¹⁷

This observation is corroborated by the XRD patterns (Figure 5) of unpromoted and Ba-promoted Cu-Cr oxide after the TPR analyses.

The intensities and peak shapes of the Cu⁰ peaks [(111) and (200) reflections at 43.5° and 50.5°, respectively] show that the Cu⁰ aggregates are much larger for the unpromoted sample. High-temperature sintering in He increases the sharpness of the Cu⁰ XRD peaks and thus the crystallite size. As the results in Figure 5 show, there is an indirect relationship between Cu⁰ crystallite size and catalytic activity. This Cu⁰ particle-size effect is related to the nature of the Cu⁰ sites on the small Cu⁰ crystallites and not the number of Cu⁰ sites. The small temperature dependency for H₂ chemisorption is more indicative of H₂ chemisorption on group 8 metals such as Rh or Pt, which chemisorb H₂ in a nonactivated manner to form a somewhat hydridic

H species (18). Since hydrides are stronger reducing agents than heterolytically dissociated H_2 , typically associated with metal oxides, a lower activation energy for CH_3OH formation is not unexpected for the promoted Cu-Cr oxides.

We conclude, therefore, that in addition to Cu^+ , which is required for CO chemisorption, metallic Cu^0 centers are required for facile H_2 chemisorption and subsequent reduction to form CH_3OH over Cu-Cr oxide.

Acknowledgments. We thank Dr. Henry Gysling for providing the $LaRhO_3$ and $GdCoO_3$ samples and for helpful discussions concerning their preparations.

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Figure 2. Rh 3d XPS of LaRhO_3 as a function of pretreatment.

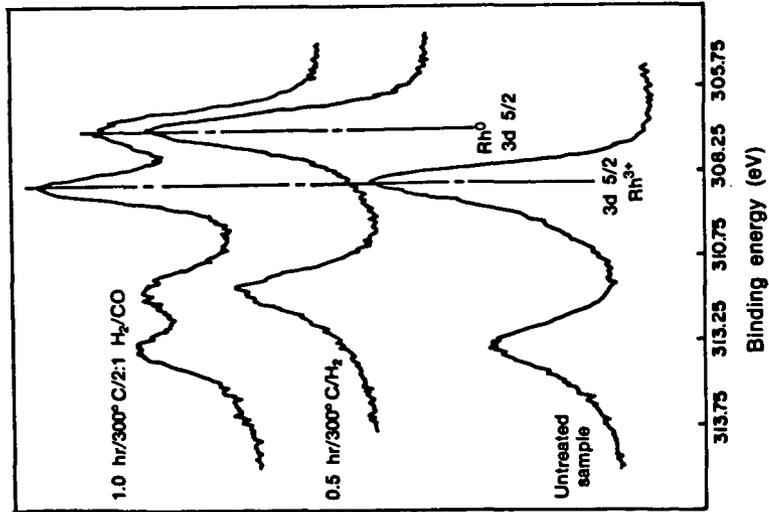


Figure 1. Temperature-programmed reduction in flowing H_2 of LaRhO_3 and GdCoO_3 . Heating rate = $10^\circ\text{C}/\text{min}$.
Sample weights: $\text{LaRhO}_3 = 100 \text{ mg}$, $\text{GdCoO}_3 = 350 \text{ mg}$.

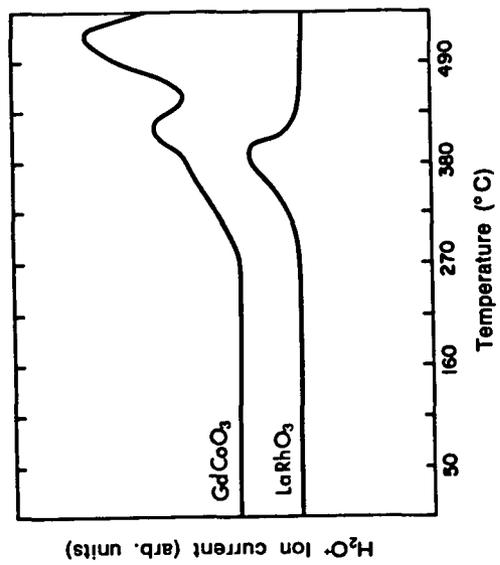


Figure 4. Fischer-Tropsch activity of reduced $GdCoO_3$. Reaction conditions: 250 °C, 800 psig overall pressure, 1:1 H_2/CO ; catalysts pretreated for 1 h at 280 °C in 1 atm of flowing H_2 .

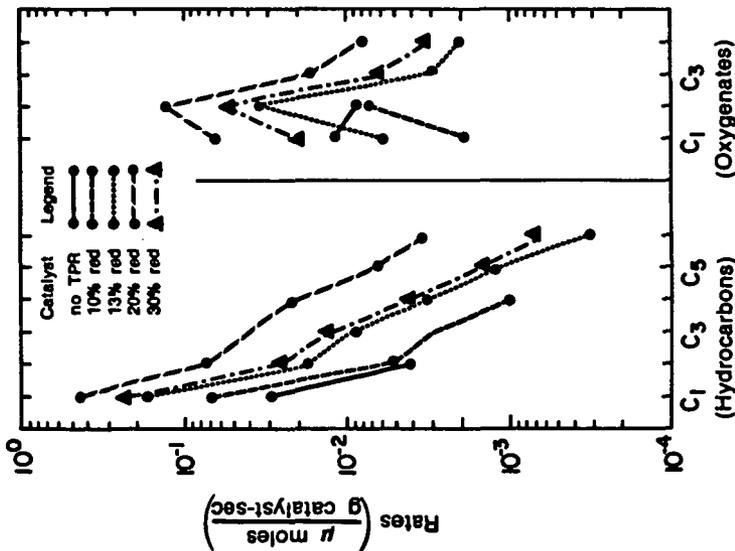


Figure 3. Fischer-Tropsch activity of $LaRhO_3$ as a function of temperature.

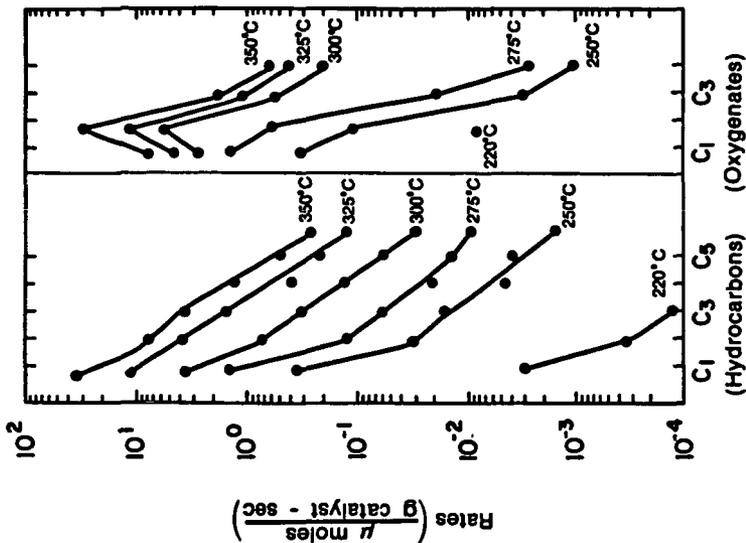
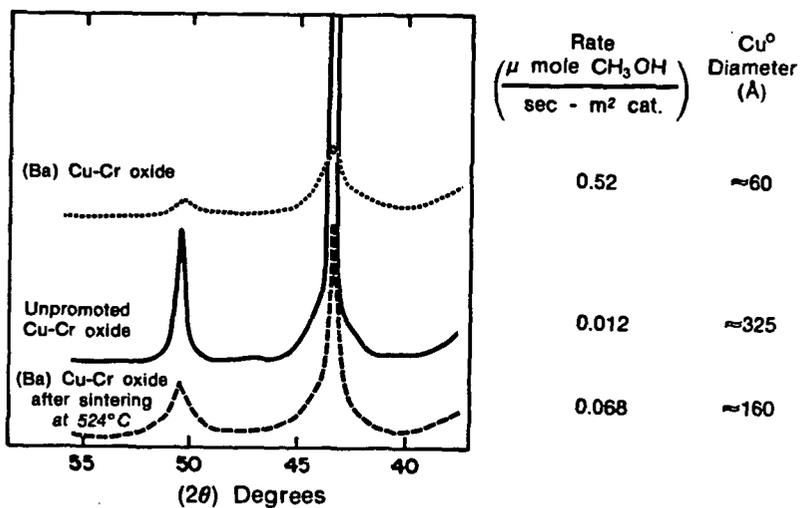


Figure 5. X-ray diffraction patterns after TPR and sintering.



METHANOL SYNTHESIS STUDIES USING IN SITU FTIR SPECTROSCOPY

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Annual methanol demand in this country has been projected to double during the 1980s to 8 million metric tons due mainly to rapid expansion in several developing applications (1). Major uses for methanol are the production of formaldehyde, dimethyl terephthalate (DMT), methyl methacrylate, methyl halides, methyl amines, and acetic acid. Large quantities of methanol are used as a gasoline blending agent and as a solvent. Legislated reductions in the amount of tetraethyl lead allowed in gasoline have increased the demand for octane boosters such as methyl tert-butyl ether (MTBE) which is made from methanol and isobutylene. The recent development of a single-step catalytic distillation process (MTBE plus) which eliminates the methanol recovery section of the conventional process, provides an economically attractive alternative to isobutylene alkylation for octane enhancement (2). Methanol by itself can be used as an octane booster, but there are problems with methanol/gasoline mixtures due to their higher affinity for water, higher evaporative losses, and the need to modify the engine.

Future demand for methanol could expand multifold as coal assumes a greater proportion of our energy needs. Although methanol is presently economically unattractive as a substitute for gasoline, the State of California has begun a program to operate 550 vehicles with methanol because it produces fewer pollutants than gasoline. More than 300 privately-owned vehicles, converted by Future Fuels of America, Inc., are running on methanol in the Sacramento, San Francisco, and Los Angeles areas. Even if gasoline remains the major automotive fuel into the next century, methanol production could increase significantly if technology such as Mobil Oil's M-Gasoline process is used to produce gasoline. This process uses a zeolite catalyst (ZSM-5) to convert methanol into a blend of paraffins, cycloparaffins, and aromatics with a research octane number of 93, i.e., an unleaded premium gasoline (3). New Zealand will use this technology to convert natural gas into approximately 12,500 bbl/d of gasoline. Utilities using coal gasification technology for power generation will probably also manufacture methanol. During off-peak hours, part of the syngas would be converted to methanol and stored; during peak hours, the methanol would be used as fuel in gas turbines to meet the high electrical demand. And finally, there is great potential for future development of methanol as a primary feedstock in the chemical industry, especially as supplies of ethylene and propylene decrease. An example is the manufacture of acetic acid, where methanol has replaced ethylene as the primary feedstock in new technologies by BASF and Monsanto (4).

The key development in methanol synthesis technology has been the catalyst. Improvements in catalyst performance are usually obtained by trial-and-error methods: variations in composition or preparation technique are tried until a catalyst is found having greater activity, selectivity, or stability. Characterization of physical and chemical properties is often incomplete, and the reasons for the superiority of a particular catalyst are frequently unclear. Although methanol synthesis as a commercial process is fully developed, the specific function of the catalyst and the fundamentals of the elementary surface reactions are still highly speculative. The main objective of this investigation has been to prepare several different compositions of methanol synthesis catalysts and characterize these catalysts by physical and chemical techniques, placing emphasis on the use of Fourier transform infrared (FT-IR) spectroscopy to identify the chemical species adsorbed on the catalyst surfaces under methanol synthesis conditions. It should be emphasized that this study has focused on the FT-IR characterization of adsorbed surface species under in situ conditions with the objective of obtaining a better understanding of the molecular interactions occurring on the catalyst surface.

In spite of advances in the characterization of methanol catalysts, the nature of adsorbed species and of the elementary surface reactions continues to be uncertain. Several mechanisms for methanol synthesis have been proposed in recent years. A chemical trapping technique has identified formate and methoxy species on a used methanol catalyst (5); the proposed methanol synthesis mechanism postulates that formate, methyloxy, and methoxy groups are reaction intermediates bonded through oxygen to a metal ion site. A much different mechanistic proposal was suggested by Herman and co-workers (6) involving carbonyl, formyl, hydroxycarbene, and hydroxymethyl intermediates bonded through carbon to a Cu(I) ion in the zinc oxide phase. Adjacent zinc ions were the centers for hydrogen adsorption. A recent revision of this mechanism has incorporated hydroxyl, formate, formyl, and methoxy species bonded to a Cu(I) ion in the reaction pathway (7). Other mechanisms have been proposed incorporating both carbon-bonded and oxygen-bonded intermediates in methanol synthesis. A reaction scheme with carbonyl, formyl, formaldehyde, and methoxy intermediates adsorbed on Cu(I) active sites within the zinc oxide lattice was developed from a review of the literature (8). This mechanism was analogous to methanol synthesis by homogeneous catalysis. Another mechanism has proposed that an oxygen vacancy acts as an active site in methanol synthesis (9). After a carbonyl species is hydrogenated to a formyl species, the oxygen on the formyl interacts with an adjacent electron-deficient vacancy. As further hydrogenation occurs, a methoxy species is formed as the bonding between the oxygen and vacancy is strengthened while the bonding between the carbon and metal ion weakens. The variation in catalytic activity with specific crystal planes of zinc oxide has been ascribed to the relative number of defects (vacancies) in each type of plane (10,11).

The catalysts were prepared by coprecipitating a mixture of metal nitrates with ammonium bicarbonate at 60°C according to the method described by Stiles (12). After filtering and washing with distilled water, the precipitates were dried in air at 115°C for 12 h and then calcined in a stream of oxygen at 400°C for 8 h. The amount of cupric oxide in these catalysts was restricted to no greater than 10% CuO due to the strong infrared absorption by cupric oxide.

The oxidic form of the catalyst was prepared for transmission infrared studies by pressing powder under a load of 4500 kg into a wafer approximately 0.10 mm thick and placing the wafer into the infrared cell. Catalyst activity and selectivity evaluations were conducted in a fixed-bed tubular reactor containing a bed of broken catalyst wafers surrounded by SiC particles. Dry nitrogen gas was flowed through the infrared cell or reactor for approximately 12 h at atmospheric pressure and 200°C to desorb water on the catalyst surface. Under these conditions there was no significant dehydroxylation of the catalyst surface. All experiments were conducted in a continuous flow mode at 60 cm³/min (STP) using high-purity gases. Water or formic acid solution could be introduced into the feed system at low concentrations by bubbling the gaseous flow through the liquid which was contained within an enclosed stainless-steel vessel (saturator). Catalysts were reduced by exposing the oxide to a 95/5 N₂/H₂ stream for 1 h at 200°C and 1 atm (pretreatment 1).

Binary catalysts with low copper contents (Cu/Zn \leq 0.15) were satisfactory for transmission infrared studies in both oxidized and reduced states. During high-pressure *in situ* studies these catalysts had a significant transmittance loss at lower wavenumbers, requiring that the identification of adsorbed species be based on infrared bands above 2000 cm⁻¹.

The adsorption of carbon monoxide on a 95/5 Zn/Cu catalyst at 200°C and 50 atm is shown in Fig. 1. The initial oxidized surface (Fig. 1a) had residual hydroxyls (bands at 3663, 3620, 3560, and 3455 cm⁻¹) and carbonates (bands at 1515, 1469, 1376, and 1323 cm⁻¹). Prolonged exposure to CO reduced the catalyst (Fig. 1b), indicated by the formation of the hydroxyl band at 3250 cm⁻¹. Formate groups (bands at 2969, 2878, 2731, and 1573 cm⁻¹), a zinc hydroxyl (band at 3520 cm⁻¹), and a zinc hydride (band at 1660 cm⁻¹) gradually developed. After 24 h (Fig. 1c) an adsorbed formaldehyde species (bands at 2935, 2834, and 2731 cm⁻¹) had formed and the

carbonyl band had shifted to 1975 cm^{-1} . (The band of gaseous CO at 2143 cm^{-1} masked the carbonyl band in the earlier spectra.)

The hydrogenation of surface species was accelerated by incorporating hydrogen into the carbon monoxide feed. Figure 2 shows the adsorption of a mixture of carbon monoxide and hydrogen ($\text{CO}/\text{H}_2 = 9/1$) on a 95/5 Zn/Cu catalyst at 200°C and 50 atm. Formate groups (band at 2879 cm^{-1}) and hydroxyls associated with reduction (band at 3252 cm^{-1}) were quickly formed (Fig. 2). The development of methoxy groups (bands at 2934 and 2822 cm^{-1}) (Fig. 2c) was accompanied by the disappearance of the isolated hydroxyls (bands at 3660 and 3612 cm^{-1}). The formate band shifted significantly from 2879 to 2868 cm^{-1} , due to the development of the methoxy groups.

The adsorption of a stoichiometric 2/1 H_2/CO mixture on 95/5, 90/10, and 85/15 Zn/Cu catalysts at 200°C and 50 atm after an hour of exposure is shown in Fig. 3. Very little detail could be observed at lower wavenumbers because of low transmittance. This surface condition would be representative of the adsorbed species during methanol synthesis. The spectra showed the hydroxyl of reduction (band at 3252 cm^{-1}), methoxy groups (bands at 2933 and 2822 cm^{-1}), and formate groups (bands at 2865 and 1575 cm^{-1}) in addition to the band for gaseous carbon monoxide at 2143 cm^{-1} . The spectra of the 85/15 Zn/Cu catalyst was noisier than the other spectra because its transmittance was an order of magnitude lower than the others.

Methanol synthesis from a stoichiometric feed of carbon monoxide and hydrogen was compared with other feed mixtures. Figure 4 shows the nature of surface species on a 95/5 Zn/Cu catalyst at 200°C and 50 atm for various feed compositions that were previously established from reactor studies to be satisfactory for methanol synthesis. A feed mixture of 66/27/7 $\text{H}_2/\text{CO}/\text{CO}_2$ produced surface species that were identical with those using only H_2 and CO in the feed. The additional band at 2350 cm^{-1} was absorption by gaseous carbon dioxide. A feed mixture of 50/50 H_2/N_2 containing some formic acid solution (73% HCOOH , 27% H_2O) also produced formate (band at 2870 cm^{-1}) and methoxy groups (bands at 2935 and 2820 cm^{-1}). Because the feed had some water and a low formic acid concentration, the isolated hydroxyls (bands at 3660 and 3620 cm^{-1}) were not completely displaced by methoxy groups.

The ternary Zn-Cu-Cr oxide catalysts, which were also restricted to low copper contents, were superior to the binary catalysts in high-pressure infrared experiments because the transmittance remained high throughout the mid-infrared range. Better surface detail provided more information for identifying adsorbed species during methanol synthesis conditions.

The reaction of carbon monoxide and hydrogen on a 90/5/5 Zn/Cu/Cr catalyst at 200°C and 50 atm is shown in Fig. 5. The initial surface species on the reduced catalyst (pretreatment 1) after exposure to a 2/1 H_2/CO mixture (Fig. 5) were formate groups (bands at 2963 , 2872 , 1582 , 1381 , and 1360 cm^{-1}), adsorbed formaldehyde species (bands at 2934 and 2843 cm^{-1}), and methoxy groups (bands at 2934 and 2824 cm^{-1}). The adsorbed formaldehyde species disappeared and the amount of methoxy groups reached a maximum in an hour (Fig. 5b), followed by a gradual decrease in methoxy groups (Fig. 5c). A pressure drop to 1 atm (Fig. 5d) revealed an adsorbed carbonyl species at 2010 cm^{-1} .

The reaction of carbon monoxide and hydrogen ($\text{H}_2/\text{CO} = 2/1$) on a 80/10/10 Zn/Cu/Cr catalyst (pretreatment 1) at 200°C and 50 atm is shown in Fig. 6. The initial spectrum (Fig. 6a) showed formate groups (bands at 2870 , 1576 , 1381 , and 1360 cm^{-1}), methoxy groups (bands at 2932 and 2822 cm^{-1}), and a carbonyl species at 2089 cm^{-1} . The methoxy groups reached a steady-state condition within an hour (Fig. 6b). The carbonyl species shifted from 2089 to 2021 cm^{-1} (Fig. 6c). A pressure drop to 1 atm (Fig. 6d) revealed in sharper detail a carbonyl species at 2010 cm^{-1} .

Reactor tests established that although a binary catalyst was active for formic acid hydrogenation to methanol, the 80/10/10 Zn/Cu/Cr catalyst was inactive for this

reaction during the same operating conditions. The adsorption of formic acid solution (73% HCOOH, 27% H₂O) in a carrier gas of 50/50 H₂/N₂ on a 80/10/10 Zn/Cu/Cr catalyst (pretreatment 1) at 200°C and 50 atm is shown in Fig. 7. A carbonyl species (band at 1983 cm⁻¹) and minor amounts of formate groups (bands at 2872, 1580, 1381, and 1360 cm⁻¹) were the only adsorbed species formed within the first hour of exposure (Fig. 7b). Some methoxy groups (bands at 2934 and 2818 cm⁻¹) were produced after prolonged exposure (Fig. 7c), but the concentration was low since the isolated hydroxyls (bands at 3668 and 3618 cm⁻¹) were not completely displaced. Thus the poor methanol synthesis activity of Zn-Cu-Cr catalysts when using formic acid in the feed mixture was due to the difficulty of formic acid decomposition into formate groups and adsorbed hydrogen at high pressures.

Information about the sequence of reaction steps and adsorption sites was obtained from transient experiments. Despite the low activity of these catalysts at 200°C, the infrared spectra showed that steady-state surface conditions were quickly reached when a 2/1 H₂/CO feed mixture was used. The surface reactions could be slowed by decreasing the amount of hydrogen in the feed mixture. Even in the extreme case of having only carbon monoxide in the gas phase, gradual hydrogenation of surface species occurred because the residual hydroxyls were a source of hydrogen. This demonstrated that hydrogen (possibly as protons) was mobile on the surface at 200°C. Formate groups were clearly formed before formaldehyde and methoxy groups. The order of formaldehyde and methoxy formation at high pressure was difficult to establish because the intensity of the formaldehyde bands was low, but results from the atmospheric studies (13) suggested that the formaldehyde species was the precursor of the methoxy species.

The spectra of Zn/Cu/Cr ternary catalysts during methanol synthesis conditions provided the most detailed information on surface species. At steady state the 80/10/10 Zn/Cu/Cr catalyst had mainly methoxy groups, some formate groups, and no observable formaldehyde groups on the surface (Fig. 6). The adsorbed carbonyl had shifted from 2089 to 2021 cm⁻¹, indicating a weakening of the carbon-oxygen bond without changing the nature of the carbonyl (linear bonded). Unfortunately, the hydroxyl region was too distinct to detect any band at 3520 cm⁻¹.

The steady-state spectrum of surface species on a binary catalyst during methanol synthesis using a feed with formic acid was very similar to the spectra for feed mixtures of CO/H₂ or CO/CO₂/H₂ (Fig. 4). Because the spectrum from the formic acid experiment showed no carbonyl species or gaseous carbon monoxide, the evidence for a reaction sequence involving formate and methoxy intermediates was strengthened. A reaction pathway involving carbon-bonded intermediates is unlikely since the lack of formate decomposition provides no carbon monoxide for this synthesis route. Alternatively, a ternary catalyst was unsatisfactory for methanol synthesis using a feed with formic acid. The infrared spectra showed very little formate and methoxy groups on this catalyst, apparently because formic acid decomposition was difficult at these conditions.

The various zinc sites proposed to be involved in this mechanism can be associated with specific crystal planes of zinc oxide (14). The isolated hydroxyls (bands at 3665 and 3620 cm⁻¹) are on the same sites as formaldehyde and methoxy species. These isolated hydroxyl sites (Zn_γ) have been associated with polar ZnO surfaces (15). The formate groups occupy a portion of the hydrogen-bonded hydroxyl sites (Zn_β) which have been associated with nonpolar ZnO surfaces. The hydrogen-bonded hydroxyls have bands at 3550 and 3450 cm⁻¹. The site of hydrogen adsorption (Zn_α), which produces a hydroxyl band at 3520 cm⁻¹, is proposed to be a stepped surface between polar and nonpolar planes of zinc oxide.

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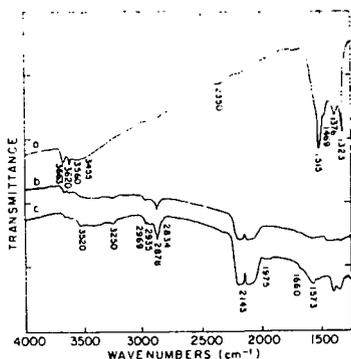


FIG. 1. Carbon monoxide adsorption on 95/5 Zn/Cu oxide at 50 atm and 200°C. (a) Oxidized surface (without pretreatment), (b) exposure for 8 h, and (c) exposure for 24 h.

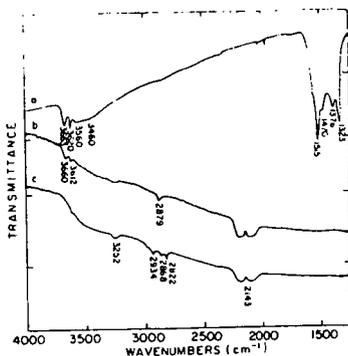


FIG. 2. Adsorption of CO-H₂ mixture on 95/5 Zn/Cu oxide at 50 atm and 200°C. (a) Oxidized surface, (b) exposure for 15 min, and (c) exposure for 1 h.

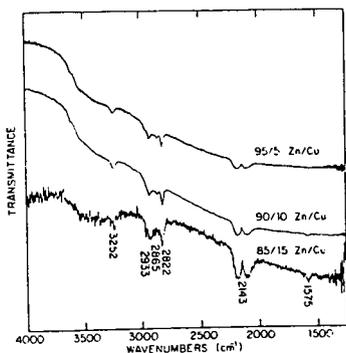


FIG. 3. Adsorption of CO-H₂ mixtures on binary oxides at 50 atm and 200°C.

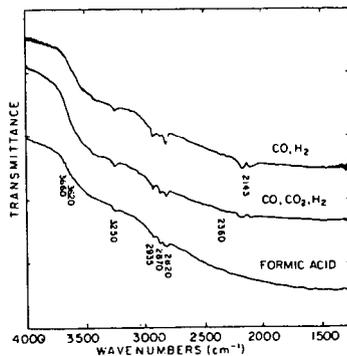
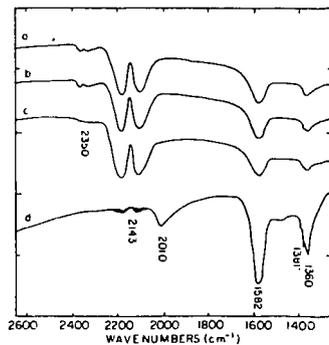
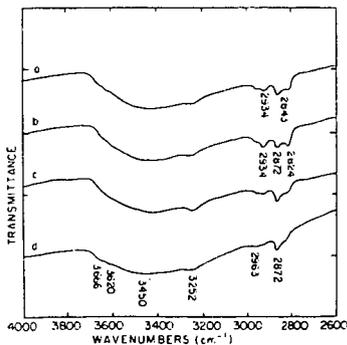


FIG. 4. Adsorption of various feed mixtures on 95/5 Zn/Cu oxide at 50 atm.



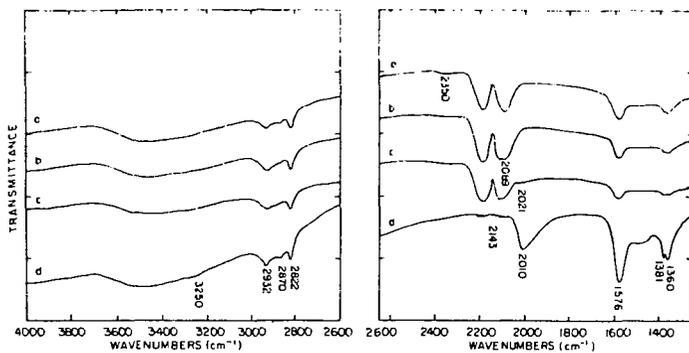


FIG. 6. Adsorption of CO-H₂ mixture on 80/10/10 Zn/Cu/Cr oxide at 50 atm and 200°C. (a) Exposure for 15 min. (b) exposure for 1 h. (c) exposure for 4 h. and (d) after pressure drop.

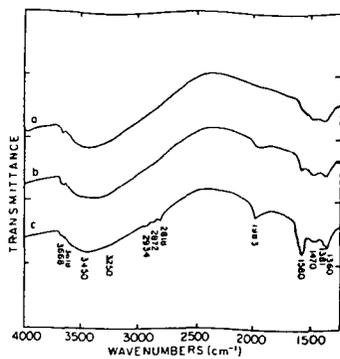


FIG. 7. Adsorption of formic acid on 80/10/10 Zn/Cu/Cr oxide at 50 atm and 200°C. (a) Reduced surface. (b) exposure for 1 h, and (c) exposure for 3 h.

ACTIVE SITES IN THE CARBON OXIDE HYDROGENATION ON OXIDE CATALYSTS

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Methanol synthesis by the hydrogenation of carbon monoxide or carbon dioxide has been a subject of intense research recently. Substantial amount of work has been performed on the prototype of the commercial copper-zinc oxide catalyst to address the questions of the nature of the active site and the reaction mechanism [1]. Methanol can also be produced either catalytically or by stoichiometric reactions on simple oxides. Natta has summarized the early work using various ZnO catalysts [2]. He reported that ZnO of different preparations exhibit different catalytic activities and selectivities. Unfortunately, these catalysts were not well characterized by today's standard, and they also contained impurities. Thus it was not possible to identify the importance of surface structure from those data.

Recently, the methanol synthesis reaction has been studied more extensively on a number of oxides, including ZrO_2 and ZnO. On these two oxides, one particularly interesting observation is that pretreatment of the oxides by a CO and H_2 mixture greatly enhances the methanol production rate from CO in the case of ZrO_2 [3], and from CO_2 in the case of ZnO [10]. Unfortunately, these catalysts undergo deactivation. In fact, deactivation is so severe on ZnO that methanol is considered to be produced by a stoichiometric and not a catalytic reaction.

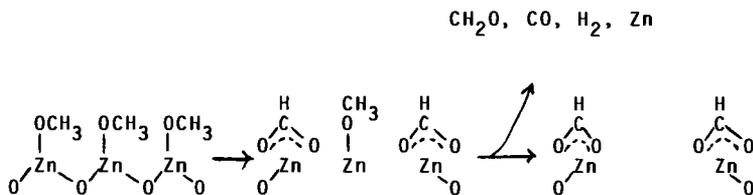
Insight into the nature of the active site on ZnO that interacts with CO or CO_2 is obtained from the study of the decomposition of methanol and 2-propanol. When methanol was decomposed on single crystal ZnO surfaces using temperature programmed decomposition technique, it was found that the Zn-polar face is the most active surface [4]. This observation has been later substantiated by the catalytic decomposition of 2-propanol on different crystal planes of ZnO [5]. The turnover frequencies at 455°C and the activation energy of this reaction are shown in the following table:

Surface	Turnover frequencies at 455 C, $\times 10^{-3} \text{ s}^{-1}$	Eact, kcal/mole
Zn-polar	1.5	11.7
stepped nonpolar	0.4	9.6
O-polar	0.35	8.4

Although similar catalytic measurements on methanol decomposition have not been made, the similarity in the mechanism between 2-propanol dehydrogenation to acetone and methanol dehydrogenation to CO, and the fact that a similar trend in reactivity is observed in temperature programmed

decomposition of both alcohols suggest that a similar trend should be expected in the catalytic decomposition of methanol.

On the Zn-polar surface, the decomposition of methanol proceeds in two separate pathways: a dehydrogenation pathway that leads to the production of formaldehyde, CO and H₂, and an oxidation pathway in which an adsorbed methoxy is first oxidized to formate which then decomposes to H₂, CO, CO₂, and H₂O. Recent data further show that metallic zinc is desorbed together with the dehydrogenation products [6]. It is postulated that the desorbed Zn originated from a surface site that is reduced during the oxidation of adsorbed methoxy into formate according to the scheme:



The above scheme is derived for the methanol decomposition reaction. It should be applicable to the methanol synthesis reaction because of microscopic reversibility. Both CO and CO₂ have been shown to be active in the hydrogenation reaction [7], and formate has been postulated to be a reaction intermediate. Formate can be formed by the insertion of CO into surface hydroxyl, and by the hydrogenation of CO₂. There is controversy as to the relative importance of these routes [8]. Based on the discussion above, one may postulate that the active site on ZnO composes of a region containing some reduced Zn surface ions. The reaction cycle for CO₂ hydrogenation proceeds as: (i) carbon dioxide is adsorbed on the site next to the reduced Zn ion; (ii) H₂ is adsorbed on the reduced Zn ion; (iii) the adsorbed CO₂ is hydrogenated to a formate; (iv) the reduced Zn ion is oxidized by the formate, which is hydrogenated to a methoxy; (v) the methoxy is hydrogenated to methanol; (vi) the active site is regenerated by reducing the site with CO and/or H₂.

For CO hydrogenation, the active site may be simply the reduced surface Zn ions. In this case, the reduced site or the anion vacancies associated with it acts as the CO adsorption site as well. The reaction may proceed as in the mechanism proposed earlier [9].

It is interesting to note that it has been reported on both ZnO [10] and ZrO₂ [3], pretreatment of the catalyst in a CO and H₂ mixture greatly enhances their activity in methanol production. Such pretreatment is more effective than H₂ alone. The results mentioned earlier on ZnO show that methanol is particularly effective in reducing the oxide. It becomes likely that such pretreatment serves to generate a large density of reduced surface sites, which are the active sites for methanol production.

The discussions above on the role of surface defects may be generalized to other reactions. It has been reported that mechanically polished single crystal surfaces of ZnO can be reduced by adsorbed CO much more readily than cleaved or grown surfaces [11]. Presumably, mechanical polishing introduces surface defects that are not easily removable by thermal annealing. Clearly, these defects have a different oxidizing and reducing power than ions on an atomically smooth surface. It may not be surprising that on oxides, surface imperfection is the active site for catalysis.

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INTEGRATED COAL GASIFICATION COMBINED CYCLES (IGCC)
AN EMERGING COMMERCIAL OPTION FOR THE POWER INDUSTRY

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Introduction

The very successful initial operation of the 100 MWe Cool Water Coal Gasification Combined Cycle Power Plant during 1985 has stimulated a great deal of interest in IGCC technology within the U.S. and foreign electric power industries. The Cool Water plant has clearly shown that IGCC plants, based on Texaco Partial Oxidation technology, can greatly reduce environmental emissions from coal utilization facilities and simultaneously meet normal electric utility load following requirements. In addition, inspections of Cool Water components, after nearly 7000 hours of operation, have shown that critical units are withstanding the service conditions very well. As a consequence, electric utilities are now developing confidence that such systems can be operated and maintained with little change in normal utility practice.

In parallel, electric load growth in the U.S. has been spurred by economic recovery and electric end use substitution; therefore, electric utilities are again beginning to plan unit additions for the early- to mid-1990's. Since many electric utilities have excess baseload capacity, initial generation additions are likely to be combustion turbines or combustion turbine combined cycle power plants. It is likely that these systems will first be used for peaking and mid-range duty and be fired with premium fuels such as natural gas and distillate. However, in the longer term, they are likely to be phased into baseload operation utilizing coal gasification technology. It is this planning flexibility which adds another important benefit and "degree of freedom" to IGCC power plants.

As a consequence, Potomac Electric Power Company has announced that it is considering the addition of a 350-400 MWe phased IGCC plant at the Dickerson Station. Virginia Power Company is proceeding with a full 200 MWe commercial module IGCC plant for repowering their Chesterfield Station. At least ten other electric utilities are currently conducting or planning site specific IGCC plant designs.

Although it is too early to judge the ultimate penetration potential of IGCC power plants in the U.S., it appears that this option may become the leading new coal technology for the 1990's.

Coal Gasification Systems Status

Development of a number of advanced coal gasification systems has been progressing at a rapid pace. Uncertainty regarding conventional fuels, i.e., natural gas and oil, environmental regulations that represent increasingly tight standards, and uncertainty regarding nuclear power deployment in a number of countries has spurred commercial development of coal gasification systems for diverse applications such as electricity generation; fertilizer, hydrogen and organic chemicals production; generation of hot water for district heating; etc.

Characterization of Gasification Systems

Coal gasification systems are usually classified by the type of gasifier which contacts and reacts coal with an oxidant (air or oxygen) to produce the desired fuel gas. If the system is blown with air, the fuel gas is low Btu gas and if the system is blown with oxygen, the fuel gas is medium Btu gas.

Three types of contacting devices are:

- o moving beds
- o fluidized beds
- o entrained beds

In moving beds a descending bed of coal, usually 1/8 to 1 inch in size, is fed by a pressurized lockhopper system to the top of a shaft. Reactant gaseous oxygen (or air) and steam enter the bottom of the vessel. As coal descends it is devolatilized, then pyrolysis reactions occur and finally carbon is gasified. The raw product gas contains tars, and oils which need to be condensed and removed. The ash may be withdrawn as a dry solid or as molten slag. In some moving bed versions, tars, oils, and coal fines are recycled to extinction.

In fluidized bed reactors, coal is ground to produce a fluid bed grind (ca 8 mesh or less). The oxidant gas (and some steam) are introduced through a perforated deck or grid at the bottom of a vessel. The flow rate of the reactants is high enough to suspend the coal particulates but not blow them out of the vessel. A uniform temperature is obtained by the mixing that occurs. Depending on the temperature, tars and oils can be avoided but fines carryover and ash slugging limit conversion of some coals to 80%-90% of the carbon. In order to overcome this limitation, the carbon containing ash can be processed in an additional vessel or the unconverted carbon can be recycled to the gasifier.

In entrained flow systems, a relatively fine grind of coal (ca 75% through 200 mesh) is fed either as a dry solid or as a water and coal mixture to a short residence time reactor. Contacting with the oxidant is achieved by means of a nozzle arrangement. At the high velocities and temperatures used in entrained systems (2000 to 3000°F) no tars or oils are produced. Carbon burn-out is nearly complete and the product gas is essentially carbon monoxide and hydrogen.

In the U.S. and abroad, advanced coal gasification technologies have been under development for the last decade. Several technologies have been supported by EPRI's program.

1. Texaco technology, represents an entrained system that features a coal water slurry feeding the pressurized, oxygen-blown gasifier. It is the farthest advanced in that three commercial or demonstration plants are in operation. Two of these plants are located in the U.S. and one in Japan. A plant in the Federal Republic of Germany will start up in late 1986 to produce organic chemicals and hot water for district heating. Projects have also been announced for China and Sweden.
2. Shell coal gasification has under construction a 250/400 ton/day pilot plant at their research center in Deer Park, Texas that will lead to commercial designs in the late 1980s. The Shell process features a dry fed entrained gasifier system that operates at elevated temperature and pressure. Current studies with U.S. electricity companies are defining commercial opportunities.
3. The British Gas Corporation and Lurgi GmbH have jointly developed a slagging, moving bed gasifier system. A commercial gasifier prototype (600 ton/day) will be started up at Westfield, Scotland in early 1986. Virginia

Power is considering installation of a coal gasification system for a 200 MWe IGCC power plant based on the BGC/Lurgi technology.

4. An air-blown rotary ported kiln (similar to a moving bed device) is under development by Allis Chalmers Corporation. A 600 ton/day prototype is located at an Illinois Power Co. power station.

The Dow Chemical Co. is installing a 160 MWe IGCC plant in Louisiana that will produce electricity and synthesis gas for industrial chemicals. Details of the system are proprietary, but the system features a coal water slurry fed entrained gasifier. Price supports of \$620 million from the Synthetic Fuels Corporation have been obtained for the project.

Other gasification systems technologies have been evolving, including the Kellogg Rust Westinghouse gasifier and Institute of Gas Technology U-Gas system that are representative of ash agglomerating fluid bed systems. Advanced fluid bed systems are also being developed in Japan. A Winkler demonstration fluid bed system operating at elevated temperature and pressure is being started up in the Federal Republic of Germany by Rheinesche Braunkohle. The Winkler system will handle 700 tons/day of coal to produce industrial chemicals and electric power.

Other projects that are at the pilot plant stage of development include a 50 ton per day pressurized pilot plant by GKT-Krupp. The Vereingete Elektrizitätswerke Westfalen (VEW) has started up a 250 ton per day pressurized pilot plant that partially converts coal (60% conversion) to low Btu gas for power generation. Lurgi has gasified lignite in an atmospheric pressure circulating fluid bed in their 15 ton per day pilot plant in Frankfurt, West Germany.

In Japan, several pilot plant programs are also underway including development of a molten iron gasification system. A 250 ton per day pilot plant is under construction in Sweden by Sumitomo-KHD in which sulfur is captured in the slag.

Combustion Turbines

Development of advanced combustion turbines is proceeding rapidly. Efficiency of combined cycle equipment is increasing from the ability to operate at higher firing temperatures. In utility applications, firing temperatures of 2,000°F are conventionally used and higher temperatures of 2,300°F can be expected before 1990. Developments in the areas of reheat, materials, and advanced cooling methods promise additional improvements in efficiency in the 1990's.

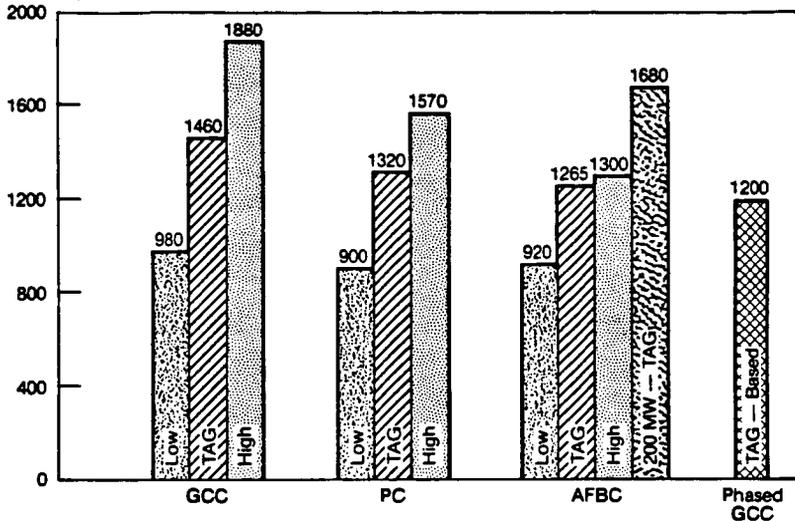
Economics of IGCC Power Plants

The three major candidates for advanced coal utilization in the 1990s are integrated coal gasification combined cycle (IGCC) power plants, atmospheric fluidized bed combustion (AFBC) systems, and improved pulverized coal (PC) power plants. In order to assess the relative benefits of IGCC, AFBC, and PC plants, EPRI in conjunction with numerous engineering/construction firms have estimated the expected range of capital and busbar power costs for such plants using 3.5% sulphur Illinois bituminous coal. Figure 1 shows a comparison of the estimated range of capital costs from various studies placed on as consistent an estimate basis as possible. The estimates shown are low and high estimates, as well as those shown in EPRI's Technical Assessment Guide (TAG) for the three competing technologies. Also shown for the IGCC plant is the benefit of utilizing phased construction of the plant rather than committing all plant capital at once. The expected cost of a 200 MWe AFBC unit has been included because it is unclear whether single 500 MWe AFBC units can be constructed. In general, there is little difference in the expected range of capital costs for these three plant types, with perhaps a small capital advantage to AFBC and PC plants.

**CAPITAL INVESTMENT ESTIMATES FOR SINGLE 500 MW UNITS
AFBC HAS ONE 200 MW UNIT CASE**

FIGURE 1

Total Capital — Constant 1985 \$/kW



**COST OF ELECTRICITY ESTIMATES USING
TAG ECONOMIC CRITERIA**

FIGURE 2

Cost of Electricity (30 year levelized) in Constant 1985 mills/kWh

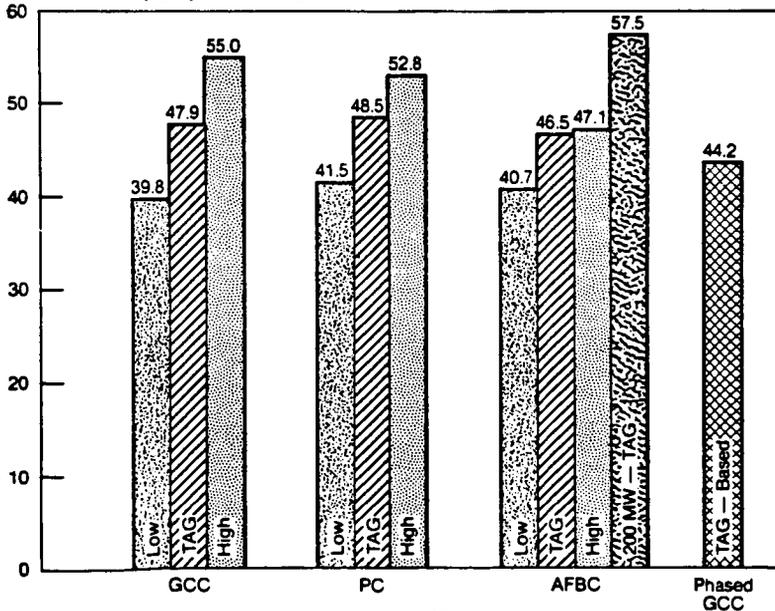


Figure 2 compares the 30 year levelized, constant 1985 dollar busbar energy costs for these same alternatives. As may be seen, all 500 MWe plants are projected to produce power costs of approximately 4¢/kWhr to 5.5¢/kWhr. There is no clear advantage for any of the technologies, considering the present uncertainties in these cost estimates. Phased construction of IGCC plants does show promise of producing some reduction in power costs.

It is in the area of environmental emissions control that coal gasification combined cycles demonstrate their true benefits. Table 1 shows typical effluent streams from the three coal-based technologies, using a 3.5% sulphur Illinois coal. The IGCC plant emits approximately one-tenth the acid rain precursors (SO₂ and NO_x) than a pulverized coal plant and produces 40 percent of the solid wastes from a PC plant. In comparison, the AFBC plant emits about 50 percent of the acid rain precursors from a PC plant, but produces 60 percent more dry solid waste for disposal. Although solid waste disposal costs were factored into the previous electricity estimates, very low costs for disposal were assumed. In many areas of the U.S., there just is not landfill area available for such large amounts of waste.

Table 1
Typical Effluent Streams
From Coal Based Power Plant Types
(Using 3.5% S. Illinois Coal)

<u>Plant Type</u>	<u>SO₂ Emissions (Tons/MWe Yr)</u>	<u>NO_x Emissions (Tons/MWe Yr)</u>	<u>Solid Wastes (Tons/MWe Yr)</u>
Pulverized Coal Plant (Precipitators Only)	140	25	240
Pulverized Coal Plant With FGD (90% Removal)	14	8	750
Integrated Gasification Combined Cycle Plant	0.14-4	3	300
Atmospheric Fluidized Bed Combustion	7	4	1200

Therefore, we believe that coal gasification combined cycle power plants show the greatest potential for meeting stringent emission control requirements, yet remaining economically competitive with alternative coal technologies.

Phased Construction of IGCC Power Plants

The modular structure of IGCC power plants provides utility companies with a major flexibility not available to them in the past. The capability to "phase-in" a plant in relatively small increments would allow a utility to more closely match load growth requirements by bringing a sequence of combustion turbines on line (shown in Figure 3 as Phases 1 and 2); converting these turbines into a combined cycle plant in Phase 3 and finally adding the gasification facility in Phase 4. The excess capacity at any time is shown as the crosshatched areas in Figure 3. This can be compared to the addition of an unphased, substantially larger power plant depicted in Figure 4. It is evident from Figures 3 and 4 that at any point in time, the phased addition approach results in substantially less excess system capacity than the conventional unphased plant construction approach. This means

FIGURE 3

PHASED CAPACITY ADDITION

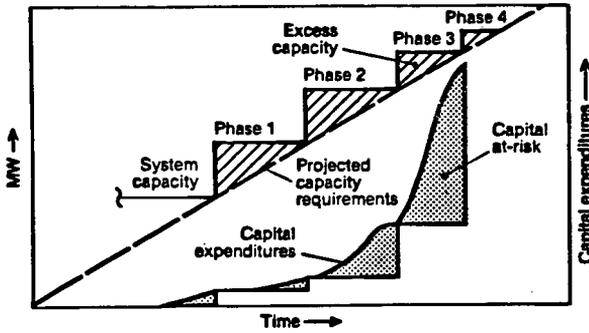
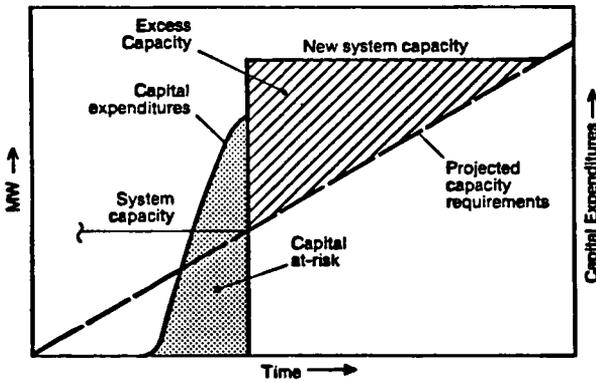


FIGURE 4

UNPHASED CAPACITY ADDITION



that the rate payer does not have to pay for unnecessary capacity ahead of time and the electric utility company does not have to place "at-risk" for an extended period of time the vast amount of capital required to construct a large, unphased power plant.

The major potential benefits to be associated with the phased addition of IGCC power plants are summarized below:

- o It allows the utility to delay and stretch out large capital outlays by more evenly matching load growth requirements without taking the full cost penalty of diseconomy of small scale.
- o It minimizes "at-risk" capital due to short construction periods for modules, i.e., capital becomes part of the rate base significantly earlier. A combustion turbine can be installed in approximately one year whereas it could take up to five years to construct a large coal-fired steam plant.
- o Phased construction provides the flexibility to take advantage of "low-cost" and "available" fuels for as long as this situation persists, i.e., a utility does not have to predict fuel prices or availability ten or fifteen years into the future. The phased plant can switch to coal whenever appropriate.
- o Phasing in an IGCC power plant provides a utility the flexibility to respond rapidly (and, therefore, at minimum cost) to changes in system load growth and/or fuel prices.
- o Finally, this procedure provides the potential for the utility to take advantage of non-utility company ownership of the coal gasification plant, thereby dramatically reducing the capital required for new capacity additions.

These potential benefits to be associated with the phased construction of IGCC power plants have already been recognized by major equipment suppliers and utilities alike. General Electric (GE) has investigated the system expansion benefits of phasing in an IGCC power plant (a procedure that they have termed PROGEN) instead of constructing conventional coal-fired steam plants. Sixteen scenarios of load growth and fuel prices were investigated. The GE results indicated that for all sixteen cases, fixed charges and production costs were significantly reduced due to phased construction. Capitalized savings for the phased construction approach ranged from \$350/kW to \$800/kW.

Potomac Electric Power Company (PEPCO) has conducted a preliminary phased construction study (comparing one IGCC plant to a coal-fired steam plant). Results of this study show a cumulative present worth saving in revenue requirements of approximately \$100 million attributable to the phased IGCC plant. Approximately one year ago, ten member companies (see Table 2) of the Utility Coal Gasification Association began an evaluation of the benefits of phased construction of IGCC plants on their systems. Preliminary results of some of these studies have confirmed the potential for financial benefits that have been claimed for this phased construction approach.

IGCC power plants clearly show promise of being the truly environmentally benign, economically competitive method of utilizing high-sulphur coal for power generation in the 1990's and beyond.

Table 2

Phased IGCC Construction Study Team

Baltimore Gas & Electric Co.
Cleveland Electric Illuminating Co.
Consumers Power Co.
Illinois Power Co.
Nevada Power Co.

Northeast Utilities
Potomac Electric Power Co.
Public Service Electric & Gas Co.
Virginia Power Co.
Public Service of Indiana

COMMERCIALIZATION OF THE DOW GASIFICATION PROCESS

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Introduction

In 1979 The Dow Chemical Company authorized \$450 million of capital to be spent on the Gulf Coast Power Conversion Project, the largest single power project Dow had ever built. This capital was to be spent phasing out less efficient gas-fired boilers at the Texas and Louisiana Divisions and integrating 910 MW of new gas turbine generation capacity into these manufacturing locations. Fuel cost savings were projected to be \$200 million per year. Future plans involved utilization of Dow's extensive lignite holdings and then-developing gasification technology to provide our Gulf Coast manufacturing locations with low-cost energy on a long-term basis. Dow completed the installation of the gas turbine facilities in 1982.

Now, after Dow's largest single research and development project ever, a price guarantee from the Synthetic Fuels Corporation has provided the incentive to build our first commercial gasifier in Plaquemine, Louisiana, the Dow Syngas Project. Western coal will be transported by rail to the plant site and the product, medium Btu syngas, will be used to fuel existing gas turbines. The output of this facility will be equivalent to 155 MW of net power production.

Background

Dow's products are highly energy intensive. The primary demand for electrical energy is derived from electro-chemical processes and thermal (steam) demand comes from production of petrochemicals and plastics. Most of our manufacturing locations have a convenient balance between electrical energy and thermal energy, allowing the economical cogeneration of power and steam. Variations of combined cycle plants to match a particular site's requirements for power and steam now exist at all of Dow's major production locations. In the U.S. alone Dow has 1600 MW of gas turbine generation capacity and 800 MW of steam turbine capacity. Over \$500 million has been spent in the last decade on power generation facilities.

History of Dow Gasification Process

Dow's current energy program took form in the early 1970's. The prospect of future shortages of natural gas and resultant high prices launched a "war on Btu's". The outcome was an energy strategy based on:

1. Gas turbines as the most efficient power production technology.
2. Solid fuels as the most abundant low cost energy resource.

Coal gasification was the necessary link to insure the viability of our strategy.

We looked at commercially available processes and found none that met our criteria. We needed a process that was:

1. Reliable.
2. Energy efficient.
3. Environmentally clean.
4. Capable of handling all coals.

Shortcomings of these processes included:

1. High capital cost.
2. Need for coal feed drying.
3. Difficult heat recovery due to tars and oil in product gas.
4. Inability to acceptably process coal feeds containing fines.

Research continued and we found processes that were not commercially proven had some very promising attributes:

1. Reduced residence time in reactor.
2. Feed flexibility.
3. Molten slag removal.
4. Environmentally clean.

However, this technology was not efficient on low rank coals and did not meet Dow's acceptable reliability criteria.

Our development efforts were then greatly expanded and by 1979 we had in place at Plaquemine, Louisiana, an air-blown 400 ton per day demonstration gasifier and a 12 ton per day pilot plant. The pilot plant was used for advanced studies. In August of 1981 we achieved an event without precedent--the successful use of synthetic gas from a coal gasification unit to fuel a 15 MW commercial gas turbine generator.

During 1981 and 1982 a new reactor design and a novel energy recovery technique were developed at the pilot plant. The pilot plant was increased in size to 36 tons per day and converted from air to an oxygen blown process. In 1983 a new technology demonstration gasifier was completed. It incorporated all the technology developed at the pilot plant and has a 1600 ton per day capacity. The capacity of the Dow Syngas Project, our first commercial scale unit, on Western coal is approximately 24000 tons per day. Consequently, scaling up from our new technology demonstration gasifier is a relatively small increment.

Description of the Dow Gasification Process

The Dow gasification process utilizes a pressurized, entrained flow, slagging, slurry fed gasifier with a continuous slag removal system. The process includes a unique heat recovery system which provides high efficiency on low rank coals. The novel slurry feed technology and continuous slag removal technique eliminates high maintenance, problem-prone lockhoppers for introducing the coal to the gasifier or for removal of slag. The design completely prevents the combustion gases and raw product gases from escaping into the atmosphere during slurry feeding or slag removal.

The coal slurry is fed to the reactor and mixed with oxygen in the burner nozzles. The feed rate of oxygen is carefully controlled to maintain the reactor temperature above the ash fusion point to insure slag removal. Under these conditions, the coal is almost totally gasified by partial combustion to produce synthetic gas

consisting principally of hydrogen, carbon monoxide, carbon dioxide, and water. The sulfur is converted almost totally to hydrogen sulfide with small amounts of carbonyl sulfide. The gasifier system operates in such a manner that essentially no tars, oils, or phenols are produced. The Dow Gasification Process includes a unique heat recovery system which provides high efficiency on low rank coals. The ash is fused in the flame, direct quenched in a water bath and removed from the bottom of the reactor as a slurry through a special pressure reducing system. The slag is dewatered and stored.

The gas exiting the gasifier system is further cooled by a conventional heat recovery boiler to near its saturation. The high pressure superheated steam produced can be used for power generation via steam turbines or to drive the oxygen plant air compressor.

The raw synthetic gas goes through a cyclone separator where most of the entrained particles are removed. Final particulate removal is achieved by water scrubbing the partially cooled gas. All of the particulates removed by the cyclone and wet scrubber are recycled to the gasifier.

The scrubbed syngas is then cooled through a series of heat exchangers before entering the acid gas removal process. The amount of low level heat recovery is economically balanced with the heat requirements of both the gasifier and the acid gas removal process.

The acid gas removal from the syngas stream is an economic evaluation of the application of several known technologies with the environmental and process constraints of the location. The particulate-free syngas from the Dow gasifier is suitable feed for any of the known commercial processes.

The Dow Syngas Project gasifier satisfies its location requirements with a Gas/Spec ST-1 acid gas removal system and a Selectox sulfur conversion unit.

Commercial Application of the Dow Gasification Process

Synthetic gas produced from the Dow gasification process can be used as a substitute for coal, natural gas, fuel oil, and natural gas derived chemical feedstock. The synthetic gas can be used as fuel for gas turbines, industrial and utility boilers, furnaces, and process heaters. It also can be used to meet some chemical feedstock demands; methanol and ammonia are examples of products which could use this synthetic gas as feedstock.

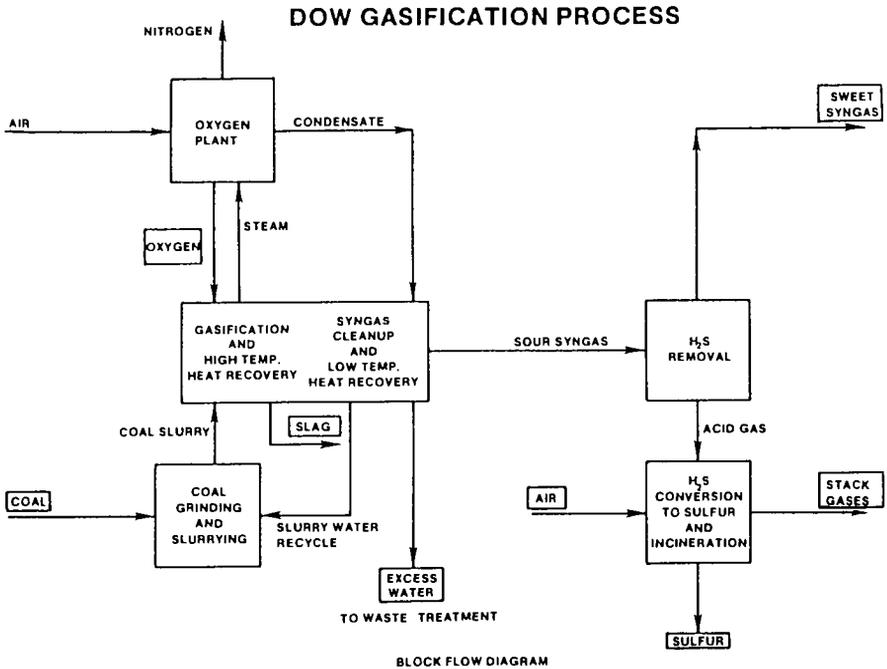
The most promising market for this synthetic gas is as fuel for turbines to generate electricity.

The combined cycle gas turbine fired by medium Btu synthetic gas has capital advantages versus coal-fired steam boilers and steam turbines. Overall energy efficiency for the medium Btu synthetic gas/combined cycle turbine is projected to be better than a steam boiler/steam turbine fed by coal.

The Dow Gasification Process has been developed as a module with a gasifier output sufficient to fuel a nominal 100 MW gas turbine. The net output of power after subtracting the requirements of the oxygen plant and gasifier and considering the by-product steam from an associated heat recovery unit converted to power is about 160 MW. When referring to a replicable unit using the Dow Gasification Process, Dow believes this is representative. Dow expects to build about ten of these modules in its Gulf Coast plants to provide fuel for existing gas turbines combined cycle units.

License Availability

Dow is committed to license its gasification technology on reasonable commercial terms. Dow offers related services such as engineering, consultation services, project management and operations support, all of which enhance our technology by bringing Dow's owner/operator perspective to a project.



TEXACO COAL GASIFICATION PROCESS: COMMERCIAL PLANT APPLICATIONS

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INTRODUCTION:

The Texaco Coal Gasification Process (TCGP) has been employed at several commercial scale facilities worldwide, and has matured to the point where it is now an attractive alternative for use in chemical and power facilities. The successful use of the process at existing facilities has yielded valuable performance data and operating experience which can help in optimizing the efficiency of all future TCGP operating plants. This process has been employed for the production of chemicals in the U.S., Japan and West Germany. Other TCGP chemical plants in China, Sweden, West Germany, and the U.S. are now being planned or are under construction.

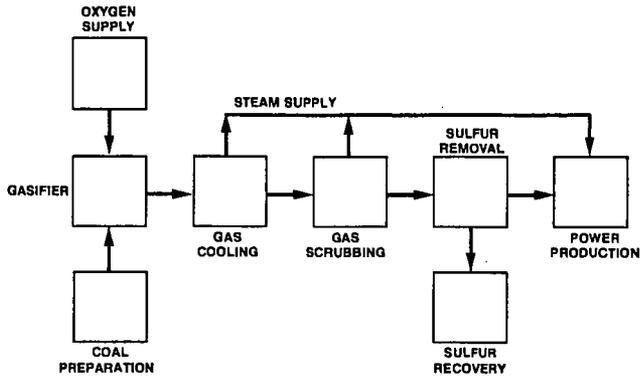
The commercial viability of TCGP for large scale production of electric power has been proven at the 120 MW Cool Water facility in Southern California. The economic and environmental characteristics of the process make it the leading technology option for future electric utility use. One major utility has publicly announced its intent to use gasification in their next power plant and many others are including it in their formal planning process.

PROCESS DESCRIPTION:

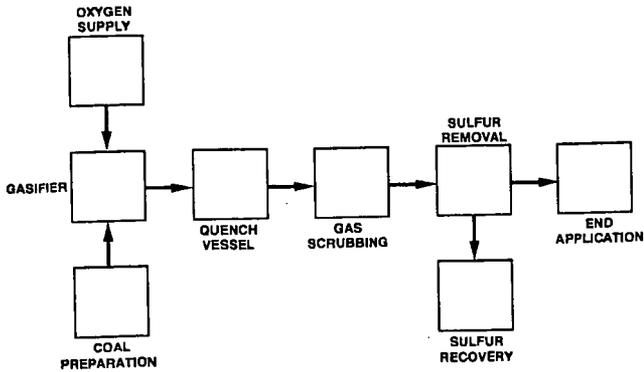
The technical details of the Texaco Coal Gasification Process will not be presented here in any depth. Numerous other papers have been published which adequately cover the details of how the process works and its technical development. (1,2,3). Figures 1 and 2 show two configurations of the process. Figure 1 shows a block flow diagram for maximum heat recovery (i.e., power plants); Figure 2 shows a minimum investment design used widely for production of synthesis gas as a chemical feedstock. Design variations from each of these options are possible to suit the requirements of a given application. For example, a gas cooler could be added to the total quench design (Figure 2) to allow for the generation of additional steam.

Utilizing Figure 1, the total process can be described. Coal is ground, slurried, and pumped to a gasifier where it reacts with oxygen. The concentration of oxygen in the gasifier is not sufficient for complete combustion, but does support partial combustion which generates heat. This heat breaks down the coal to form synthesis gas, a medium BTU product composed primarily of carbon monoxide and hydrogen. This synthesis gas is cooled, cleaned, and sent to the desired application. In Figure 1, the application is power production.

**FIGURE 1
TEXACO COAL GASIFICATION PROCESS
MAXIMUM ENERGY RECOVERY**



**FIGURE 2
TEXACO COAL GASIFICATION PROCESS
MINIMUM INVESTMENT DESIGN**



The steps between the gasifier and the desired end use employ proven commercial technology. The ash in the coal forms a slag material which is removed from the gas cooling section. This slag is a non-hazardous material suitable for landfill or other applications. The steam generated in the gas cooling process is utilized in a steam turbine for additional electric power production. After the gas is sufficiently cooled and scrubbed of particulate matter, it is directed to a sulfur removal and recovery stage. Sulfur contained in the coal is transformed primarily into H_2S , due to the gasification reactor temperature and oxygen deficient environment. This H_2S can be separated from the syngas using commercially available units. The H_2S is transformed to elemental sulfur which can be sold as a by-product.

EXISTING APPLICATIONS:

Nuclear fusion, photovoltaics, magnetohydrodynamics, coal liquefaction, wind power, geothermal energy, gasohol, and coal gasification were among the answers proposed for the energy crisis of the late 70's. The crisis is viewed differently in the mid 80's due to current energy economics. The petroleum and natural gas supply problems which caused the 1970's crises may have subsided, but they have not disappeared. In the years ahead, there will be a need for clean energy conversion from feedstocks other than oil and gas. Of the technologies listed as alternatives, only coal gasification has been proven on a commercial scale as an attractive option for chemicals and power production. Of the coal gasification designs proposed, only the Texaco process has met the necessary standards for wide spread acceptance and use.

For electric power production, the Cool Water Plant, in Barstow, California, has been operating for over a year and a half, gasifying 1,000 tons per day of coal in an integrated gasification combined cycle (IGCC) power plant. The plant's capacity factor (plant electric production/rated capacity) for 1985 was higher than the 1984 average for all conventional coal fired power generating stations of 50 MW or greater in the U.S. (4). Environmental EPA data from Cool Water has shown its performance to far surpass EPA standards, as well as being environmentally superior to other new fossil fuel power plants of equivalent size.

For production of chemicals, TCGP is becoming increasingly popular for feedstock generation. Tennessee Eastman utilizes the process for the production of acetic anhydride, which is used in the photographic industries. They recently reported a 97% on-stream factor for the final six months of 1984 (5). Ube Industries gasifies 1650 tons per day of Australian and South African coals for the production of ammonia. Commercial scale ammonia plants using TCGP are now being planned for Sweden and China. A TCGP facility for the manufacture of oxo-chemicals from coal is being constructed in West Germany.

FUTURE APPLICATIONS

Electric Power Production

Application of the Texaco Coal Gasification Process for the large scale generation of electric power is clearly on the horizon. Some utilities have publicly stated their desire to use gasification for power

production (6,7). Many others are internally evaluating the technology for power facilities to be commissioned in the 1990's. The Electric Power Research Institute has established a Utilities Coal Gasification Association to "encourage the development of coal gasification for the production of electricity..." (8). Utility membership in this group has grown steadily, and interest among utilities in the technology is keen.

The merits of TCGP must be viewed in relative terms compared to other power generation technologies. There are currently four leading methods of power generation in the U.S. These are nuclear fission, oil or gas combustion, coal combustion, and hydropower. 99.4% of all U.S. nameplate capacity for electric power generation utilizes these technologies (9). Each of these technologies, however, has limitations which restrict future usage. No new nuclear fission plant is being planned, and the last plants under construction are currently scheduled to start up in the early 90's. The social, political, and engineering factors which doomed this industry have been widely discussed and speculated upon. Oil and gas combustion are limited by the future supply of the fuel. The average age of an oil or gas plant retired from service in 1984 was approximately 31 years (10). Thus, in considering a power plant construction project, it is necessary to consider the price and availability of fuel not just today, but also in the decades ahead. Most forecasts suggest severe escalation for petroleum products within this time frame. Data Resources Inc. predicts inflation for oil and gas to average in excess of 10% per year throughout the 1990's, while coal prices will remain relatively stable in real terms over the same period (11).

As for coal, supply is adequate but environmental concerns may restrict its use in a direct fired mode. Hydropower has no limitations other than its availability. Expansion of the use of hydro requires the rivers to exist in sufficient concentrated quantities for large scale power generation. Unfortunately, such resources are not abundant. Ecological concerns also are present with the construction of hydropower facilities.

This situation indicates that revisions or new methods of power generation will be required for the future. As noted earlier, the Texaco Coal Gasification Process is the most successful alternate technology to emerge in recent years. New power generation methods must prove themselves to be fully competitive in terms of economic viability and operability on a commercial scale. The performance of Cool Water has proven the operability of TCGP, and the experience gained there will enhance the performance of future plants. The economic viability of TCGP has been attested to in various engineering studies (12).

Coal gasification is not the only viable option for power generation in the 1990's. Site specific considerations will make other technologies the preferred option in some instances. However, a certain percentage of new plants will be designed for IGCC due to its long range attractiveness. The North American Electric Reliability Council (NERC) forecasts 113,200 MW of new electricity generation capacity will be added by 1994 (13). Planned coal and nuclear plants account for much of that addition. With the halt in nuclear planning, new construction beyond 1994 will be predominately coal based. Due to the economic comparability and environmental superiority of the Texaco Process as compared with traditional coal utilization methods, this process will emerge as the technology of choice for many of the capacity additions in the 1990's.

Some traits of the plants to be built in the 1990's will distinguish them from the Cool Water facility. In efficiency, it has been estimated that a 600 MW facility could be constructed with a net heat rate of 9,000 BTU/KWH (14). This rating is competitive with efficiencies found in existing power generation facilities. Some 600 MW facilities will be built, but a recent trend in power plant construction is toward smaller size, and phased modular construction. A typical plant could be 400 MW in total size, constructed in four 100 MW phases. This allows the utility to gain an economy of scale on some components while delaying capital expenditures until they are needed. Economic efficiency of the construction process can be greatly enhanced with this phasing technique. Gasification facilities are well suited to these construction methods.

Power plants being constructed in the 1990's must have a great deal of operating flexibility. Cool Water has verified the ability of TCGP to load follow (i.e., reduce or increase output quickly) and, as noted, the capacity factor for the plant has already surpassed the competitive level. From these results, it is expected that TCGP can meet the operating requirements of a base load power station. To do so on a practical basis requires flexibility of feedstock requirements. Table 1 shows a list of coals which have been gasified at Texaco's Montebello Research Laboratory. Several are now in use at commercial scale plants worldwide. Although there are differences in gasifier operations for different coals, experience has shown that all bituminous and sub-bituminous coals, and petroleum coke can be successfully gasified.

Environmentally, the performance of Texaco coal gasification plants will probably be the standard which other fossil fuel facilities will have to meet. Furthermore, environmental records of future IGCC plants could surpass that of Cool Water, which has already been characterized as the cleanest coal burning plant in operation today. Figure 3 illustrates a comparison of actual emissions for Cool Water vs. the EPA standards. Clearly, this is a strong asset of TCGP in assessing its future use in large scale power production.

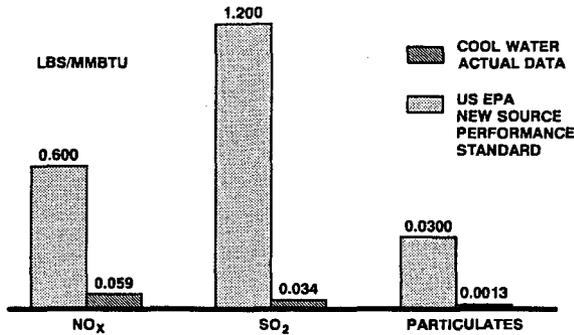
It is not certain which utilities will be among the first to begin utilizing IGCC plants. It could be expected that a need for capacity, an environmentally sensitive operating region, and a proximity to coal reserves, will be among the traits of those initial utilities. Perhaps more important is a corporate mindset which accepts business risk, and seeks to improve their operating efficiencies. Particularly attractive to such firms might be the ability of the process to co-produce other saleable products such as methanol, hydrogen, and steam.

A final aspect of future IGCC power plants which will distinguish them from those currently in service may be the ownership structure. The Public Utility Regulatory Policy Act of 1978 (PURPA) has encouraged the private ownership of electric power production facilities. The concept of power plant partnerships between utilities and power users, utilities and power industry firms, and between utilities and other utilities will become more common particularly for projects using relatively new technologies. The utility/power user partnership concept could become especially prevalent if deregulation proceeds on an aggressive course as some suggest.

CHEMICALS PRODUCTION:

The basic product of coal gasification is synthesis gas, a mixture

**FIGURE 3
ENVIRONMENTAL PERFORMANCE**



**TABLE 1
FEEDSTOCK FLEXIBILITY
SOLID FUELS GASIFIED AT
TEXACO'S MONTEBELLO RESEARCH LABORATORY**

<u>BITUMINOUS COALS</u>	<u>SUB-BITUMINOUS COALS</u>
PITTSBURGH	WYOMING
KENTUCKY 9	ARIZONA
ILLINOIS 6	UTAH
UTAH	JAPAN
TENNESSEE	<u>LIGNITES</u>
GERMANY	TEXAS
AUSTRALIA	NORTH DAKOTA
SOUTH AFRICA	GREECE
CANADA	<u>PETROLEUM COKES</u>
ITALY	FLUID
CHINA	DELAYED
	CALCINED

**FIGURE 4
CHEMICAL COMPOSITION OF
SYNTHESIS GAS - CLEAN &
DRY BASIS**

<u>COMPONENT</u>	<u>VOLUME %</u>
CO	42.5
H ₂	38.2
CO ₂	18.6
CH ₄	0.3
AR & N ₂	0.4
H ₂ S & COS	50PPM

of several components primarily carbon monoxide and hydrogen. Figure 4 shows a typical breakdown of its composition on a dry basis after cleanup. As was indicated, this gas can be used as a medium BTU fuel for the production of electrical power. It can also be used as a chemical feedstock in the production of hydrogen, ammonia, methanol, oxo-chemicals, and other substances. The growth of these industries is expected to be strong in the early 1990's (15). However, existing overcapacity for many of these products makes capacity addition forecasting difficult.

One of the key factors in assessing the prospects for TCGP in the chemicals manufacturing industries is the competition. As a chemical feedstock, synthesis gas must compete directly with natural gas. In today's market, natural gas is relatively inexpensive and supply is plentiful. The future of this market must be viewed in assessing feedstock alternatives. The popular belief among forecasters is that in the long-term, inflation rates and security of supply will be much more favorable for the consumer of coal as opposed to the natural gas user. Therefore, if a plant is being designed to securely fulfill a long term need for the plant output, coal gasification would be a preferred option.

Multi-product facilities based upon coal gasification will probably see some use in the coming years. NASA is considering the construction of a coal gasification plant to supply all of their hydrogen, oxygen, electricity, nitrogen, fuel gas, and heated water needs. Because coal, air, and water are the only feed streams needed to produce the desired products, the security of supply is not expected to be a problem. If NASA so opted, the proposed facility could also export any of the produced products as well as argon and sulfur. Such decisions would hinge upon the commercial marketplace.

Because of the many uses of synthesis gas, multi-product projects, similar to that proposed by NASA, will probably be considered in the future. In such facilities, steam, electricity, sulfur, and possibly other products will be produced. Under federal cogeneration guidelines, export electricity produced in this type of facility must be purchased by the local utility who must also supply backup power to the site.

Several types of possible chemical facilities could use TCGP for feedstock generation and cogenerated power production. Based upon the current trends in the chemicals markets, we believe TCGP will play a major role in the chemical industry by the mid-1990's. As has been true to date, no single application will dominate, but plants of varying size and product slate will be constructed.

SUMMARY:

The development of the Texaco Coal Gasification Process has now reached a stage of maturity. Already employed on a commercial scale in the chemicals and electric utility industries, the process is now being widely considered for use in the new facilities in both these sectors. Benefitting from the experience obtained in the existing plants, new facilities can expect operating efficiencies and process economics which are competitive, and in some cases, superior to other technologies.

The process not only meets the necessary economic, operational, and environmental standards for use today, it also uses technology which will

become even more attractive with future energy economics and environmental regulations. Natural gas and petroleum feedstocks are forecasted to become more expensive and more scarce. Conventional coal technology, even with scrubbers, may be subject to continuous capital outlays to meet changing environmental standards. A Texaco Coal Gasification Facility will not be as seriously affected by either of these expected trends.

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LIQUID FUELS FROM COAL DERIVED SYNTHESIS GAS

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INTRODUCTION

Modern synthesis gas chemistry has evolved from technology first developed in Germany early this century. Since that time worldwide interest in the production of liquid fuels from coal has gone through cycles reflecting the perceived availability of petroleum.

In the U.S., the Department of Energy (DOE) has supported an indirect coal liquefaction program to investigate new techniques for the production of liquid hydrocarbon and alcohol fuels. The liquid synthesis is based on utilizing a feedstock of low hydrogen content synthesis gas generated by advanced, more efficient, coal gasifiers. Research topics include improved reactor and catalyst developments as well as more fundamental studies of the reaction chemistry. This presentation summarizes results of a number of these projects and provides some comparisons with existing commercial liquid synthesis technology. Fuels of interest include gasoline, diesel and jet fuel, methanol and higher alcohols. Achievements in liquid phase synthesis of hydrocarbons and methanol are described along with the Methanol to Gasoline (MTG) process. Catalyst research is briefly reviewed and an assessment made of needs and prospects for future research.

Alcohol Fuels

Alcohols can perform well as fuels in both internal combustion and diesel engines, under appropriate conditions. Methanol is available now for evaluation as a direct replacement for petroleum derived gasoline, and the worldwide trend to low lead content gasoline provides a continuing interest in various oxygenates for use as octane enhancers in gasoline. Chem Systems, Inc. has developed a liquid phase reactor system to improve the thermal efficiency of methanol production (1). This Liquid Phase Methanol process is being further investigated under a cost shared contract in a 5 TPD process development unit (PDU) which is located at La Porte, Texas, on a site owned by the prime contractor Air Products and Chemicals, Inc. The PDU has operated very successfully with a Cu/Zn catalyst powder less than 50 microns in diameter slurried in an inert oil in the reactor through which the synthesis gas is passed. Operating conditions are 5.27 MPa (765 psia) and 250°C (482°F). During its most recent 40-day run (May-June 1985) the PDU operated with a nominal 25 wt. percent catalyst slurry and the catalyst activity declined 0.34 percent per day. The process is being developed for use with a modern coal gasifier to produce "once through" methanol to be available as a peak fuel while the unconverted gas is a baseload turbine fuel in an electric power plant. With a different feed gas (Table 1), the reactor can be used to produce "all methanol."

The production of higher alcohols requires more selective catalysts than are currently available. Union Carbide Corp. (S. Charleston, W.VA) is investigating homogeneous catalysts for this purpose under a cost sharing contract. Although existing commercial systems for production of chemicals require excessive operating pressure (20.78 MPa, 3015 psia), a successful catalyst will provide excellent selectivity and simple operations, particularly if the pressure can be

reduced. At Lehigh University modified heterogeneous Cu/Zn catalysts are being investigated in the pressure range of 3.45 MPa to 7.58 MPa (500 psia to 1100 psia) for the production of mixtures of methanol and higher alcohols. The alcohol product typically contains 40 percent methanol and about 25 percent isobutanol, for example (2).

Liquid Hydrocarbons

Historically, liquid hydrocarbons have been synthesized from hydrogen/carbon monoxide mixtures via Fischer-Tropsch technology using iron based catalysts. Another option is now being demonstrated commercially in New Zealand where methanol is produced from synthesis gas and immediately converted to high octane gasoline via the Methanol to Gasoline (MTG) process. Mobil Research and Development Corporation has developed this process based on a ZSM-5 catalyst, under a cost shared contract with DOE. A fixed bed reactor system was first developed with yields as shown in Table 2. In recent years, a more efficient fluid bed concept has been demonstrated in a 100 bpd (methanol feed) pilot plant located in West Germany. The plant operated very well at all levels including a much higher than designed throughput. Most recently operating conditions for the pilot plant were changed in order to produce light olefins rather than gasoline. The olefins can be converted commercially to diesel fuel and/or gasoline to offer the market another option. This project in West Germany has been supported equally by the U.S. Government, the W. German Government and an industrial consortium consisting of two German firms with Mobil.

Mobil also has been active in a cost-shared project using a liquid phase Fischer-Tropsch reactor followed by a second stage reactor with zeolite catalyst to produce gasoline and wax which can readily be cracked to produce diesel fuel (3) (4). Table 3 provides data on yield selectivity from the first stage in low wax mode of operation. This project provided an empirical correlation between methane and wax yields using a precipitated iron, copper, potassium catalyst. Mobil's bench scale research has also included first stage reactor operation in a high wax mode.

The base line technology against which process improvements are measured is that found at the Sasol plants in South Africa. These commercial plants owned by the South African Coal, Oil, and Gas Corp., Ltd. produce an estimated 90,000 bpd of diesel fuel and gasoline. Lurgi dry bottom coal gasifiers provide the synthesis gas while Arge fixed bed reactors, and Synthol fast fluid bed reactors, produce a broad mixture of fuels and chemicals which have to be further processed to marketable products (5).

During recent years, the MITRE Corp. McLean, VA, has put the Sasol and other process schemes on a common basis so that product costs can be compared. Table 4 provides relative costs for diesel fuel or gasoline (both having the same market value). All plants are considered to be located in the U.S. and the feed coal is Western subbituminous. For the advanced processes, the British Gas Corp. (BGC) Lurgi gasifier is used. The liquid phase Mobil two-stage process is compared with the liquid phase data reported by Prof. H. Kolbel from operations in Germany during the 1950's (4).

Catalyst Research

Practical catalysts must meet several criteria but one property has eluded researchers interested in producing hydrocarbons with more than one carbon atom. That property is selectivity to produce precisely the desired product. When one thinks of selectivity, one thinks of shape selective supported catalysts, homogeneous catalysts and enzymes or other biological approaches. While working

with a synthesis gas feedstock, one is tempted also by the possibility of combining the carbon monoxide activation/hydrogenation steps with shape selectivity in one catalyst formulation, in one reactor. All of these concepts are being investigated in a continuing research effort with the expectation that the results will better describe the reaction chemistry leading in turn to new and greatly improved catalysts.

Reactor Technology

Liquid, or slurry phase, reactors are recognized as having a potential to significantly improve thermal efficiency over more traditional reactor designs for highly exothermic reactions. A number of existing projects are investigating liquid phase reactors, but we need much more data describing the hydrodynamics of such systems under process conditions. Actual operating data are required from a reactor which can be operated in a commercially viable churn turbulent flow regime. Results from research to date are encouraging in processing a lower H_2/CO ratio syngas and producing a flexible product slate. The liquid phase Fischer-Tropsch reactor also operates at a higher, more productive, temperature (260°C-270°C) than is feasible with the Arge or Synthol reactors using the current iron catalyst at Sasol.

CONCLUSION

It is a pleasure to report, however briefly, the progress being made in new approaches to the synthesis of liquid fuels from coal derived syngas. The recently demonstrated selectivity and efficiency of producing hydrocarbon fuels from methanol is outstanding. Improvements are being demonstrated in selectivity for higher alcohol production and in making efficient use of liquid or slurry phase reactors.

Nevertheless, we have to conclude that no one has the technology today to produce liquid fuels from coal derived synthesis gas at a cost competitive with near term petroleum derived fuels in a typical industrial environment. Although the feed gas accounts for about two-thirds of the cost of the liquid fuel in a Fischer-Tropsch plant, the liquid synthesis can be greatly improved to contribute major savings. Existing technology to directly convert synthesis gas to liquid hydrocarbons is non-selective requiring extensive downstream processing. Liquid fuel production via methanol uses two selective process schemes, but they cannot be closely integrated, at present, for maximum efficiency. New approaches may provide solutions but until then we need to pursue avenues suggested by current research. A slurry reactor offers constant temperature operation with catalyst addition and withdrawal capability. Can productivity be improved with higher catalyst loading? Can wax produced in the reactor be efficiently removed and separated from the catalyst? What is the potential for new reactor designs? For continuous stirred tank reactors? Does catalyst metal particle size affect or control selectivity? Do homogeneous catalysts have any role in hydrocarbon, as distinct from alcohol, synthesis? Can practical bi-functional catalysts be developed to convert syngas to hydrocarbon liquids? Can by-product methane be converted directly and efficiently to liquid fuel?

Successful results from research efforts now underway will go far in answering these questions, and the data will be available for use by industry whenever it is required in the United States.

TABLE 1. Liquid Phase Methanol Process
Typical Reactor Feed Gas Compositions (6)

	Methanol/Power Production (CO-Rich Feed)	All-Methanol Product (Balanced Feed)
H ₂	35.0 Mole %	55.0 Mole %
CO	51.0	19.0
CO ₂	13.0	5.0
CO ₄	--	3.0
Inerts	1.0	18.0
	100.0%	100.0%
H ₂ /CO	0.69	2.89

TABLE 2. MTG Process - Typical Yields from Methanol
in Fixed Bed Reactor System (7)

Yields, wt. percent of methanol charged

Methanol	0.00
Hydrocarbons	43.66
Water	56.15
CO, CO ₂	0.04
Coke, oxygenates	0.15
Total	100.00

Yields, wt. percent of hydrocarbon product

Gasoline (including alkylate*)	85.0
LPG	13.6
Fuel gas	1.4
Total	100.0

- * 93 unleaded RO no. Without alkylate gasoline is 80.0%. Alkylate is process derived from propylene, butenes and isobutane. Reactor inlet temperature 316°C; pressure 2.17 MPa (314 psia).

TABLE 3. Mobil Liquid Phase Fischer-Tropsch
Summary of Data from Low-Wax Operation*

Yields, wt. percent product

C ₁	7.5
C ₂ /C ₂ =	1.6/3.0
C ₃ /C ₃ =	2.0/8.0
C ₄ /C ₄ =	2.1/6.6
C ₄ oxygenates	5.1
C ₅ -C ₁₁	39.4 (2.5)**
C ₁₂ -C ₁₈	14.3 (0.8)**
C ₁₉ -C ₂₃	2.9 (0.04)**
C ₂₃ ⁺ wax	7.5
Total	100.0

* Bubble column reactor, 260°C 1.52 MPa, H₂/CO = 0.67, Fe/Cu/K catalyst, 2.75 NL syngas/gFe/hr, 86 mole % syngas conversion, 800 g hydrocarbons/g Fe catalyst life.

** Numbers in parenthesis are oxygenates.

TABLE 4. Comparative Costs for Fischer-Tropsch
Synthesis (4)

Unit product cost*, market basis, all liquid output

<u>Case</u>	<u>Relative Cost</u>
Sasol (dry Lurgi/Synthol)	1.00
Modified Sasol (BGC Lurgi/Synthol)	0.83
Liquid Phase Fischer-Tropsch (BGC Lurgi/Kolbel)	0.69
Liquid Phase Fischer-Tropsch (BGC/Mobil)**	0.73

* All liquid hydrocarbon fuels valued the same.

** Upgrading of Fischer-Tropsch liquids to marketable fuels based on ZSM-5 catalyst.

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RECENT DEVELOPMENTS IN SASOL FISCHER-TROPSCH TECHNOLOGY

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When considering improvements in the Fischer-Tropsch (FT) route for producing liquid fuels from coal, it is important to bear in mind the relative costs of the various process steps. An approximate cost breakdown for a typical plant is as follows:

Synthesis gas production	58 %	(coal gasification 53 %; CH ₄ reforming 5 %)
FT synthesis	18 %	(plant 15 %; Catalyst 3 %)
Product separation	12 %	(cryogenic 4 %; Alcohols & ketones 4 %)
Refinery	10 %	(olefin oligomerization 4 %)
Diverse	2 %	

The advantage of a big improvement in the selectivity of the FT synthesis (an ideal case would be one which only produces gasoline and diesel fuel) is that this would lower the costs of both the product separation and the refinery sections, which, together account for 22 % of the total. Obvious provisos, however, are that the cost of the catalyst should not be markedly increased and that its conversion activity should remain high otherwise the gains in say the refinery would be negated by increased FT synthesis costs. Elimination of certain products do not necessarily improve the economics. If the FT process made no ethylene, the expensive cryogenic separation unit could be replaced by a cheaper process but this would not be a real gain as the market value of ethylene relative to that of liquid fuels justifies its recovery. A similar situation holds for the alcohols and ketones produced in the FT process. If these products were absent then the expensive process of first recovering them from the FT water and then refining them would significantly lower the overall costs. (Note that these products would have to be completely absent and not just lowered as the latter would have little impact on the economics of recovery as the volume of water to be processed would remain unchanged.) These low molecular mass alcohols and ketones, however, sell at high prices and furthermore the alcohols are valuable as gasoline octane boosters. Thus the production and recovery of these components are justified.

At Sasol the amount of methane produced far exceeds the need of the local fuel gas market and so the CH₄ is reformed with steam and oxygen to yield H₂ and CO which is recycled to the FT synthesis units. This reforming is of course thermally inefficient and results in a (about 14 %) loss of hydrocarbon produced from the reformed CH₄. In the Sasol process the bulk of the CH₄ comes not from Fischer-Tropsch but from the Lurgi coal gasification process and so to eliminate CH₄ reforming would require an alternative gasification process. Confining the issue to only the FT process, if a zero C₁ to C₂ selectivity could be achieved with only gasoline and diesel fuel being produced, it is estimated that the overall cost of the process could be cut by about 5 %. Because the capital outlay for a big commercial plant is huge, the 5 % saving is very significant.

To date, however, the attainment of a big improvement in the FT selectivity has been an elusive goal. All the proposed mechanisms of the reaction involve the concept of stepwise addition of single carbon entities to the growing hydrocarbon chains on the catalyst surface (1). This inevitably leads to a wide distribution of products. By manipulating the catalyst's formulation and/or the process conditions the probability of chaingrowth can be varied but the result is simply that if the production of C₁ to C₃ hydrocarbons is lowered the

production of the products heavier than diesel fuel increase. The maximum of the sum of gasoline plus diesel fuel lies in the vicinity of 60 % (1). To improve on this appears to require either a new kind of catalyst with a different mechanism or to superimpose some secondary catalytic action such as olefin oligomerization and/or wax cracking.

To date Sasol has exclusively used iron based catalysts in the FT process not only because iron is cheap but also because the products are richer in olefins than those normally produced by other metals active in the FT reaction. The lighter, C₂ to C₅, olefins are readily oligomerized to either gasoline or diesel thus giving the overall process a high degree of flexibility regarding the ratio of gasoline to diesel fuel produced. A major drawback of iron catalysts at temperatures above say 270 °C is that carbon deposition occurs. This, for mainly mechanical reasons (eg, disintegration of the particles) results in shorter reactor on-line times which means both a higher catalyst consumption rate and more reactors required per unit of gas converted. At the temperatures at which metals like cobalt or ruthenium are active in the FT synthesis, very little carbon is deposited and so these metals have attracted attention as alternative catalysts. On a unit mass basis the cost of cobalt is about 250 times that of the iron used at Sasol while that of ruthenium is about 20 000 times that of iron. To make cobalt competitive with iron, a much lower mass per volume of catalyst will have to be employed, the catalyst life will have to be longer (with its activity and selectivity as good or better than that of iron) and the spent catalyst will have to be regenerated for re-use. While these objectives may well be met with cobalt, the case for ruthenium is bleak. Putting aside the price, it can be shown that for only a single Sasol commercial plant one would require more than the entire available world stock of ruthenium to produce the needed catalyst charge which would only contain 0,5 mass % of Ru on a typical support. The production of Ru and other noble metals such as Rh, is entirely linked to the demand for Pt.

While Sasol remains committed to developing catalysts with longer lives and improved selectivities these objectives are seen as longer termed. In the short term investigations have concentrated on increasing the production per reactor, developing lower cost reactors and optimizing the product spectrum by improving the processes downstream of the FT reactors. Several of these new developments are in the process of being commercialized.

Kinetic investigations had indicated and pilot plant tests had confirmed that for both fixed bed tubular and fluidised bed reactors the production per unit volume of catalyst could be raised by simultaneously increasing the operating pressure and the volume of feed gas thus maintaining a fixed linear velocity, ie a fixed residence time in the reactors (1). Sasol recently decided to build an additional commercial fixed bed tubular reactor to increase the production of FT waxes. This reactor will operate at a pressure considerably higher than the reactors currently in use.

The Synthol reactors, which are the "work horses" of the Sasol FT process, are circulating fluidized bed (CFB) types with catalyst flowing down a standpipe on one side and up a riser on the other side (see Figure 1). These units are already very large and there are doubts whether they could be scaled up further by either increasing their diameter or raising the operating pressure. As an alternative Sasol has been investigating for some time the fixed fluidized bed (FFB) system. In this reactor the catalyst is not circulated but remains "stationary" as an ebulating bed with the gas entering at the bottom. This reactor is considerably smaller and so should be cheaper to construct, simpler to operate and increasing the operating pressure presents no mechanical problems. An additional advantage of higher pressure in the case of iron catalysts operating at high temperatures is that the rate of carbon deposition on the catalyst decreases (1) which for the reasons already mentioned, should result in longer life catalysts. A demonstration FFB unit has been operating at the Sasolburg plant for some time and various design aspects have been

investigated. The design of a large commercial size unit is currently underway for cost estimating purposes and hopefully for implementation in the near future.

Another reactor version being investigated is the slurry phase reactor. In concept this is similar to the FFB reactor but the finely divided catalyst is suspended in a suitable liquid, eg molten FT wax. Compared to the fixed bed reactor it is cheaper to construct and because of this it may be a viable alternative process for producing FT waxes. A potential advantage of the slurry phase system is that with iron catalysts it can operate in the temperature range 260 to 290 °C. In this temperature region a fixed bed would plug up due to carbon deposition while a "dry" fluidized bed would "defluidize" because of catalyst particle agglomeration due to wax formation. To date the experimental investigations at Sasol have been confined to 5 cm ID pilot plant reactors. The next planned phase is the construction of a larger pilot reactor in order to investigate the system at hydrodynamic conditions likely to exist in a commercial scale reactor.

With regards to process improvements downstream of the FT reactors two catalytic processes are being developed. FT waxes produced at low temperatures are essentially straight-chained containing no aromatics and are sulphur and nitrogen-free. Because of these factors the wax can be hydrocracked under relatively mild conditions to yield up to 80 % of high quality diesel fuel. These results have been independently verified by firms specializing in hydrocracking and no problems are foreseen in commercializing the process.

Light olefin oligomerization to gasoline and diesel fuel has been commercially practiced by Sasol for many years but the process which utilizes a supported phosphoric acid catalyst produces a light diesel fuel which has a lowish viscosity and a very poor cetane number, the latter being due to the high degree of skeletal branching. Because of this the amount of this fuel which can be added to the overall pool is limited and so restricts the full utilization of olefin oligomerization to maximise diesel fuel production. The new generation ZSM-5 type zeolites can completely remove the above-mentioned limitations. Because of the high strength of the zeolite acid sites, a higher degree of oligomerization occurs which results in a higher molecular mass product with a higher viscosity. Because of the unique size of the zeolite pores, it is physically impossible to produce highly branched oligomers and consequently the product diesel fuel has a high cetane number. This process has been thoroughly evaluated on pilot plant scale with FT feedstocks both at Sasolburg and abroad. The building of a full scale commercial plant is presently under consideration as part of a debottlenecking process at Sasol's Secunda complex. A new zeolite oligomerization plant would not only process additional olefins but should also be able to improve the yield and quality of the overall diesel fuel pool.

Table 1 illustrates the selectivities (on a carbon atom basis) typically obtained in the two types of commercial FT reactors used by Sasol, namely, the high temperature Synthol process (geared at making light olefins and gasoline) and the lower temperature fixed bed process (geared at making waxes). Applying to each of these product streams, the secondary processes previously discussed, namely, oligomerization of the C_3 to C_6 olefins to yield 75 % diesel fuel and hydrocracking of the wax to yield 80 % diesel fuel, the overall liquid fuel situation obtained is shown in Table 2. As can be seen high quality diesel fuel at high yields can be obtained in both processes. When both maximum liquid fuel yield and maximum diesel fuel to gasoline ratio is required, the low temperature Arge FT process has the greater potential.

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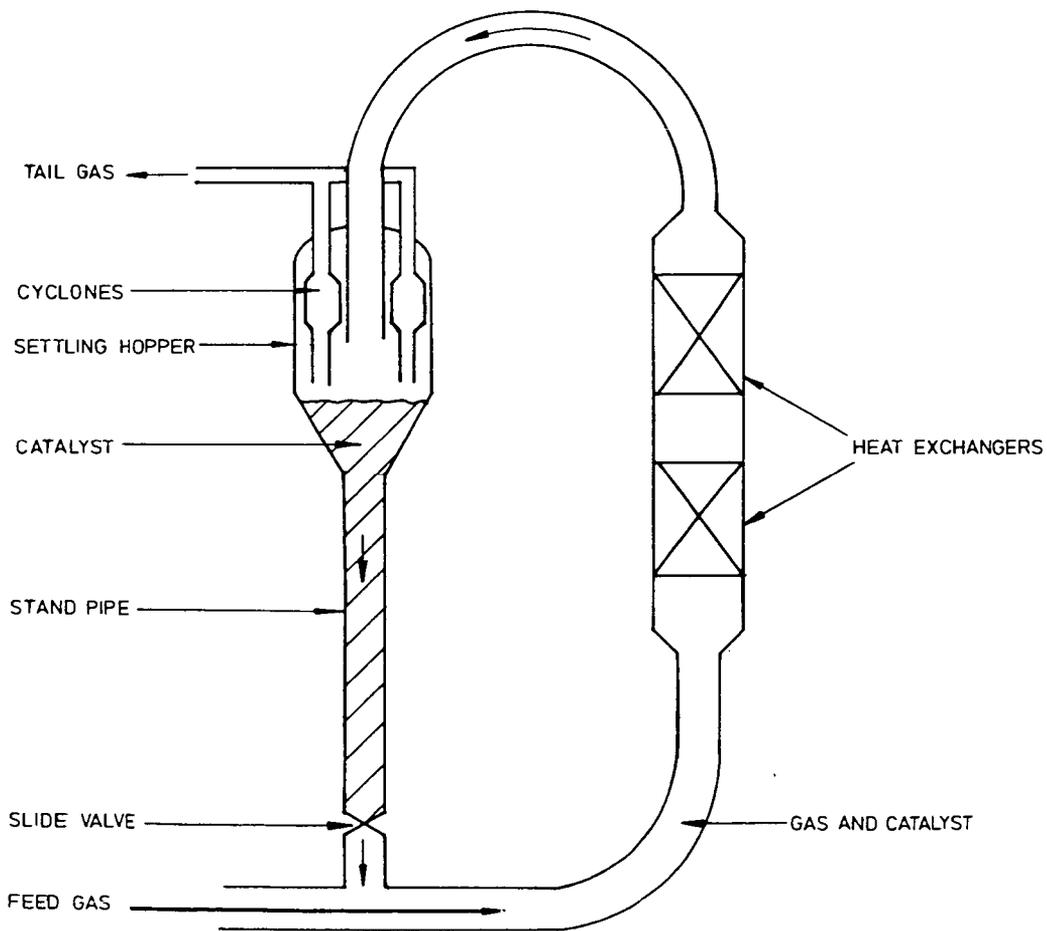
TABLE 1
COMPARISON OF THE STRAIGHT-RUN FT PRODUCTS FROM THE SYNTHOL AND ARGE REACTORS

Cut	Synthol high temperature	Arge low temperature
C ₁ + C ₂	16.0	5.4
C ₃ to C ₆ paraffins	5.0	8.4
C ₃ to C ₆ olefins	33.5	7.6
C ₇ - 160 °C	17.2	8.0
160 - 350 °C	14.0	19.5
+350 °C	7.8	48.1
Water soluble oxygenated compounds	6.5	3.0

TABLE 2
COMPARISON OF THE TWO DIESEL PRODUCING SCHEMES

Cut	Synthol	Arge
Total final liquid product	80	87
% diesel of liquid fuel	55	75
Diesel source:		
- From oligomerization	58	9
- Straight run	31	30
Wax cracking	11	61
Cetane number of diesel pool	53	67

(All figures are percentages except for the cetane number)



PRODUCTION OF SYNTHETIC GASOLINE
AND DIESEL FUEL FROM NON-PETROLEUM RESOURCES

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In late 1985, the New Zealand Gas-to-Gasoline Complex was successfully streamered producing high octane gasoline from natural gas. The heart of this complex is the Mobil fixed-bed Methanol-to-Gasoline (MTG) section which represents one of several newly developed technologies for production of synthetic gasoline and diesel fuels. All of these technologies are based on production of methanol by conventional technology, followed by conversion of the methanol to transportation fuel.

The fixed-bed (MTG) process has been developed and commercialized. The fluid-bed version of the MTG process, which is now also available for commercial license, has a higher thermal efficiency and possesses substantial yield and octane number advantages over the fixed-bed. Successful scale-up was completed in 1984 in a 100 BPD semi-works plant in Wesseling, Federal Republic of Germany. The project was funded jointly by the U.S. and German governments and by the industrial participants: Mobil; Union Rheinsche Braunkohlen Kraftstoff, AG; and Uhde, GmbH.

This fluid-bed MTG project was extended recently to demonstrate a related fluid-bed process for selective conversion of methanol to olefins (MTO). The MTO process can be combined with Mobil's commercially available olefins conversion process (Mobil-Olefins-to-Gasoline-and-Distillate, MOGD) for coproduction of high quality gasoline and distillate via methanol. This MTO process was also successfully demonstrated at the Wesseling semi-works with this project being completed in late 1985.

The key to all these processes (MTG, MTO, and MOGD) is Mobil's unique family of shape selective zeolite catalysts. It

is this shape selectivity which in MTG/MTO inhibits coke-forming reactions and in MOGD allows production of a high quality diesel range (C_{10} - C_{20}) iso-olefinic product, which is then hydrogenated to the corresponding iso-paraffins (Figure 1).

A simplified schematic of the combined MTO/MOGD process is shown in Figure 2. Methanol is fed to the MTO unit where it is converted stoichiometrically to hydrocarbons and water byproduct. The hydrocarbons are separated into MOGD light olefin feed, an ethene rich fuel gas, and an aromatic gasoline stream which is routed to final product blending. MTO light olefins are fed to the MOGD unit along with an MOGD gasoline recycle stream. MOGD product is then separated into raw distillate, gasoline, and small fuel gas and LPG streams. The raw distillate is hydrotreated at mild conditions to take full advantage of its cetane number potential. To improve liquid yield an optional alkylation unit can also be employed to react produced isobutane with light olefins.

The combined process is highly flexible and can be operated to meet seasonal variation in fuels demand (Table 1). The D/G ratio can be adjusted between zero and about 1.5 while maintaining overall single pass gasoline plus diesel yield above 90 wt % of hydrocarbons. Octane number of the finished gasoline exceeds 92 R+0 (Research, unleaded). Distillate cetane number is about 50 and is essentially independent of feedstock and D/G mix.

MTO reaction chemistry is nearly identical to that of MTG. In the simplified MTG reaction scheme (Figure 3), methanol is equilibrated to a methanol-dimethyl ether-water mixture, and then dehydrated further to a mixture of C_5 olefins. The light olefins react reversibly to heavier olefins, which convert further to aromatics and paraffins. In contrast to MTG, MTO process conditions are selected to maximize olefins yield. A small amount of highly aromatic gasoline is also produced. The light olefin fraction is an excellent feedstock for the MOGD unit.

The MTO initial process step preferentially converts methanol to light olefins and a lesser amount of aromatic gasoline having an octane number of greater than 98 R+0. Yield of C_3 olefins is 50-75 wt % of hydrocarbon, depending on process conditions.

A fluid-bed reactor configuration (Figure 4) is preferred as it permits steady-state operation at maximum olefin selectivity and complete methanol conversion. The exothermic heat of reaction can be recovered by immersing heat exchange coils

directly in the catalyst bed. Overall thermal efficiency of the MTO reactor section is estimated to be 95-96%.

The second step of this route is the MOGD process. This process reacts light olefins to the final gasoline and diesel product. In this process, gasoline and diesel selectivity is greater than 95% of the light olefin feed, and gasoline/diesel product ratios have been produced ranging 0.12 to >100. Because of the catalyst shape selectivity, most products are methyl branched iso-olefins. In the C_5 - C_{10} range, branched iso-olefins have good octane rating. In the C_{10} to C_{20} range, after hydrogenation, isoparaffins have good diesel fuel properties.

Figure 5 shows the schematic flow for a commercial MOGD plant. The preferred process flow generally uses four fixed-bed reactors, three on line and one in regeneration. The three on line are in series with inter-reactor coolers and liquid recycle to control the heat of reaction. The olefinic feed is mixed with a recycle stream and passes through the three reactors. After exiting the last reactor, fractionation is used to generate a gasoline-rich stream for recycle to the reactors. This recycle helps control the heat of reaction.

MOGD distillate and gasoline mode product yields are shown in Table 2 for comparative purposes. The charge stock, propene/butenes (C_3/C_4), represent the main olefinic components of MTO product. As shown C_3/C_4 yielded 79% diesel, 18% gasoline and only 3% light gas. Of the nonolefins in MTO product, all saturated compounds (paraffins and cycloparaffins) will pass through MOGD unreacted and thus can be left in the feed. Of the range of potential olefin feeds, C_2 to C_{10} , all give distillate and gasoline. Gasoline mode MOGD yields are also shown. If desired, a single MOGD plant can be designed to shift from gasoline to distillate mode to accommodate shifts in product demand.

Table 3 shows representative MOGD distillate product properties (after hydrotreating) compared with U.S. industry standards. As diesel, the paraffinic MOGD fuel is low density but is an exceptionally good blending stock due to its low pour point and negligible sulfur content. Vehicle testing has also shown straight MOGD diesel to perform similarly to conventional diesel fuel.

Because of its essentially pure iso-paraffinic structure, the MOGD product makes excellent Jet Fuel, meeting or exceeding all commercial and military specifications (Jet A, A-1, U.S. Military JP-4, -5 and -7).

Large Scale Testing

In late 1981, a large scale MOGD test run was made in a Mobil refinery. The test run used commercially produced zeolite catalyst in refinery scale equipment and was carried out successfully for 70 days.

The unit was a commercial wax hydrofinisher modified to duplicate a prototype design using 3 MOGD reactors. Charge stock was a mixture of propane/propene/butanes/butenes (62% olefins) pumped directly from an FCC unit. The test run had four objectives: demonstrate all modes of operation in commercial scale equipment, demonstrate controllability in a large multireactor adiabatic unit, demonstrate catalyst regenerability, and provide sufficient distillate product for fleet testing. All objectives were met, and over the 70-day run, product yields and selectivities were the same as found in our pilot plant; thus, demonstrating MOGD could be scaled up for commercial application.

The MTO process has presently been scaled up successfully in a 100 BPD fluid-bed semi-works in Germany. The 100 BPD plant was started up February, 1985 after completing modifications required to enable extended operation at MTO conditions. Plant operation was terminated in November 1985 after a successful six months on-stream program. Product yields and catalyst performance were similar to those obtained in a 4 BPD pilot plant at Mobil's Paulsboro Laboratory, under the same conditions. With completion of the 100 BPD MTO program, large scale testing is completed for both steps of the MTO/MOGD process route, completing development of a novel and efficient route to synthetic gasoline and diesel.

/njh

Table 1

MTO/MOGD PRODUCT YIELDS

Distillate/Gasoline Ratio	0.8
Product Yield, Wt %	
LPG	4.4
Gasoline	52.9
Diesel	42.7
	<hr/>
	100.0
Product Quality	
Gasoline, R+O	94.4
M+O	80.6
(R+M)/2	87.5
Diesel Cetane Number	50.0

Table 2
MOGD PROCESS YIELDS
C₃-/C₄- FEED

	<u>Max Distillate Mode</u>	<u>Gasoline Mode</u>
C ₁ -C ₃	1	4
C ₄	2	5
C ₅ -165°C Gasoline	18	-
165°C ⁺ Distillate	79	-
C ₅ -200°C Gasoline	-	84
200°C ⁺ Distillate	-	7

Table 3
MOGD PRODUCT QUALITY

	<u>MOGD Product</u>	<u>Industry Standards</u>
Diesel Fuel		
Specific Gravity, 15°C	.79	.84-.88
Pour Point, °C	<-50	-7
Cetane Number	50	45
Sulfur, Wt %	<.002	0.5 max
Viscosity, cs @ 40°C	2.5	1.90-4.1
Jet Fuel		
Freeze Point, °C	<-60	-40
Aromatics, Vol %	4	25 max
Smoke Point, mm	28	18 min
JFTOT, °C	343	260

Figure 1

SHAPE SELECTIVE REACTION PATH

MTG/MTO

Methanol → C₁₀ Paraffins, Olefins, Aromatics
 $n\text{CH}_3\text{OH} \rightarrow (\text{CH}_2)_n + n\text{H}_2\text{O}$

MOGD

Light Olefins → Gasoline → Distillate

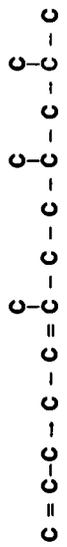


Figure 3

REACTION PATH

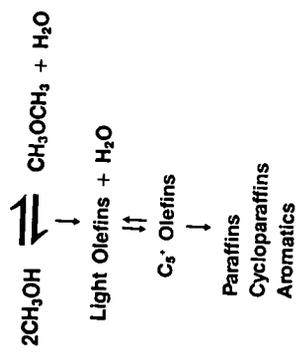


Figure 2

MTG/MOGD PROCESS SCHEMATIC

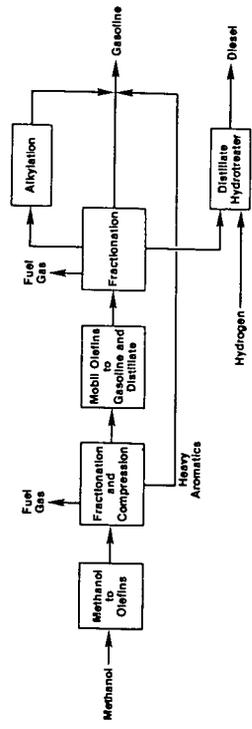


Figure 4

100 B/D FLUID-BED MTO PLANT

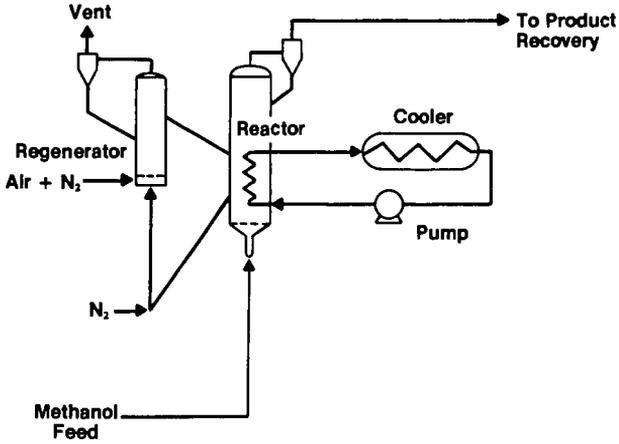
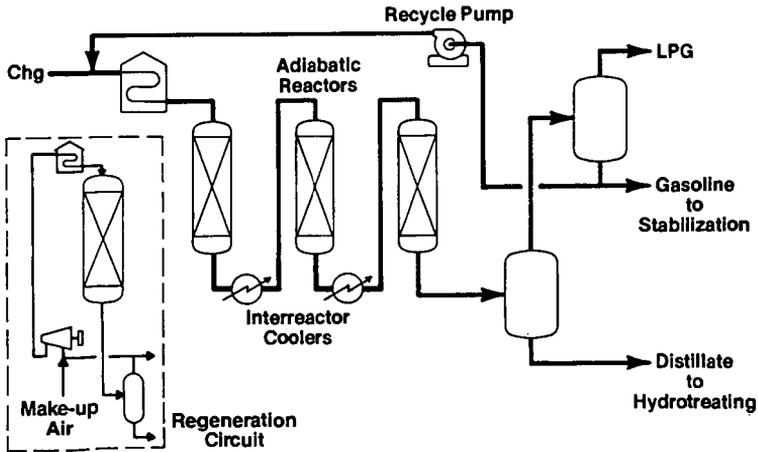


Figure 5

MOGD PROCESS FLOW Max Distillate Mode



LCI CO-PROCESSING: A FAMILY OF TECHNOLOGIES
FOR UPGRADING LOW GRADE FEEDSTOCKS

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INTRODUCTION

The Western Hemisphere and North Sea oil producers have been experiencing a serious decline in light oil production and light oil "find" rates. In spite of aggressive drilling programs, "finds" over the past fourteen years have been about 60 percent of production (1). In seeking continued production of refined petroleum products, refiners will have to consider processing of bottom-of-the-barrel feedstocks to a much greater extent. When one superimposes the additional issue of the politically-controlled availability of Mid-East petroleum supplies in the Western World, it is clear that there is a need for technology that will afford the refiner greater flexibility in feedstock selection and feedstock processability.

One potentially attractive route to satisfying these needs is the co-processing of petroleum feedstocks with other more plentiful and less costly fossil fuels. Lummus Crest Inc. (LCI) has formulated a concept for co-processing bottom-of-the-barrel oils with coal and other solid carbonaceous feedstocks to produce high quality distillate fuels. The concept is based on a two-stage approach in which the solid carbonaceous feedstocks are converted to liquid hydrocarbonaceous materials in a thermal reaction zone devoid of externally-supplied catalysts followed by catalytic hydroprocessing of the thermal stage products together with petrolea in an expanded-bed hydrotreater. The unconverted solids from the thermal reactor can optionally be removed by known solids separation techniques, such as Anti-Solvent Deashing (ASDA), prior to upgrading in the expanded-bed hydrotreater. A distillate fraction from the hydrotreater can be recycled to serve as the slurry vehicle for the solid carbonaceous feedstock.

Co-processing of heavy petroleum residua and coal has been the subject of a 33-month experimental program currently being carried out at LCI's Engineering Development Center under joint funding with the U.S. Department of Energy. Details of this work have been presented elsewhere (2,3). Currently, we envision a common reaction system that can co-process petroleum residua with other carbonaceous feedstocks, such as oil shale and biomass, in addition to coal.

LCI CO-PROCESSING FLOWSCHEMES

With current refinery technology, heavy petroleum residua characterized by high metals content and high coking propensity can be processed by either carbon-rejection technology such as delayed or fluid coking; by hydrogen-addition technology such as fixed-bed or expanded-bed hydrogenation; or by combinations thereof. Two co-processing applications based on hydrogen-addition technology are disclosed here.

With current commercial residuum hydroprocessing technologies, conversion is limited to about 50 to 60 percent to IBP-524°C (975°F) distillates. The unconverted resid from the hydrotreater is either processed further in a coker to recover additional distillates and a coke product or blended off with available low sulfur fuels. The unconverted residuum that has been subjected to catalytic hydrogenation has potentially good properties as a solvent for liquefaction of coal, biomass and oil shale.

Figure 1 is a schematic flow diagram of a co-processing scheme for utilizing the unconverted resid from a residuum hydrotreater. The short contact time (SCT) thermal reactor system has been demonstrated at the 300 kg/day (1/3 tpd) scale in LCI's Integrated Two-Stage Liquefaction (ITSL) process development unit (4) as well as at the 5448 kg/day (6 tpd) scale at the Wilsonville pilot plant (5), both on coal products only. The SCT concept is predicated on the fact that the rate of activation of fossil-derived oil precursors is relatively fast with respect to the rate of hydrocracking of these intermediate products to all distillate products. On this basis, the ITSL process "decouples" the primary fossil liquefaction step from the secondary hydrocracking step. Accordingly, we have projected that there will be capital cost savings in a commercial plant in which the primary liquefaction step is carried out in a relatively low-cost, fired-coil reactor system as compared to a larger, high pressure soaker-reactor system. Furthermore, the more capital-intensive catalytic step could then be optimized to hydrocrack the extracts without being constrained by the need to simultaneously solubilize the solid carbonaceous feedstock.

An alternative co-processing application is shown schematically in Figure 2. This application is predicated on the following factors:

- o The feedstock cost of liquid products from the hydroliquefaction of coal, oil shale and biomass is significantly less than that of petroleum as seen from the following table:

Table 1

<u>Feedstock</u>	<u>Typical Liquids Yields</u>		<u>Typical Feedstock Transfer Price</u>			<u>Feedstock Cost of Raw Liquids</u>	
	10 ³ M ³ /Kg	g/t	\$/kg	\$/ton	\$/MM Btu	\$/M ³	\$/Bbl
Bituminous Coal	0.70	168	0.033	30	1.25	47	7.50
Kentucky Shale	0.10	24	0.004	4	0.68	44	7.00
Wood Chips	0.50	120	0.022	20	1.40	44	7.00
Municipal Solid Wastes	0.25	60	0.009*	8*	0.85*	(35)	(5.60)

* Denotes tipping fee paid by solid waste collector.

(): Denotes credit for MSW feedstock against product liquids.

o A raw syncrude can probably be generated in a thermal reaction system, such as an SCT heater, at an incremental cost competitive with that of imported petroleum crude when the conversion units are constructed and operated on an over-the fence basis adjacent to a large petroleum refinery.

o There is good indication that there will be a beneficial synergism during catalytic hydrotreatment when co-processing synfuels products from an SCT reactor with vacuum residua. The synergism may take the form of increased distillate yield and/or improved desulfurization/demetallization at conventional hydrocracking operating severities.

o There should be no significant deterioration of the hydrogen content-molecular weight relationship (Stangeland surface) of the distillate products when the syncrude content of the combined feed to the hydrocracker is less than about 20 percent (6).

DEVONIAN SHALE RESOURCES

The Devonian oil shale resource of the Kentucky-Ohio-Tennessee region of the U.S. has the potential of providing a significant percentage of our refinery feedstock needs. Until recently, U.S. oil shales were considered unsatisfactory resources because of their relatively low oil yields in the Fischer Assay test and in conventional retorting. Fischer Assay oil yields per unit weight of organic carbon obtained with the Devonian marine shales have been less than half of those obtained from the Eocene lacustrine shales (Green River formation) of Colorado, Utah and Wyoming. The shale resources recoverable by surface mining in the Lewis and Fleming County, Kentucky region alone could generate shale liquids

corresponding to about 12,000 M³/day (750,000 bbl/day) for 20 years.

Previous efforts (7,8) have clearly demonstrated that hydrogen addition or hydrotreating technologies can result in significantly higher oil yields from Devonian shales than can be achieved by thermal retorting technologies, on the order of 200 to 250% of that of Fischer assay. These studies also concluded that a commercial-scale application of hydrotreating technologies has potentially favorable economics.

However, without some type of government subsidy, a grass-roots shale conversion facility still cannot compete on the open market with current petroleum prices. The LCI co-processing concept represents a possibly nearer-term economic reality when applied in an over-the-fence relationship with an interested refiner. By way of example, assume an existing hydrocracker is processing a virgin resid priced at \$157/M³ (\$25/bbl). For the case of a 8584 M³/day (54,000 Bbl/day) unit, if we back off 20% feed or 1717 M³/day (10,800 Bbl/day) and replace this by 1717 M³/day (10,800 Bbl/day) of shale liquids, then there should be no significant deterioration of the distillate product characteristics. In other words, the co-processing liquids should respond in conventional downstream refinery processing units essentially similar to that of the straight run petroleum-derived liquids. With oil shale priced at \$0.004/Kg (\$4/ton) and resid at \$157/M³ (\$25/bbl), the differential cash flow available for a) amortizing the capital equipment associated with shale preparation, spent shale disposal and the SCT reaction system and b) operating costs is estimated to be about \$64MM per year. Assuming 20% capital charges and operating costs (ex. shale) of \$0.006/Kg (\$5.75/ton) (8), this cash flow would correspond to an installed capital cost for the upstream shale processing equipment of about \$140 MM.

Some preliminary screening tests were made in the batch autoclave reactor system at LCI's Engineering Development Center. The tests simulated the SCT reaction system in which the oil shale samples were first extracted under short-contact-time conditions. This was followed by blending of the SCT products with an Arab Heavy vacuum residua and hydrotreatment in an LC-Fining^(SM) simulation test unit. The results of these tests will be reviewed at the Symposium.

(SM) LC-Fining is a service mark of Lummus Crest Inc. for engineering, marketing and technical services related to hydrocracking and hydrosulfurization processes for reduced crude and residual oils.

BIOMASS RESOURCES

Biomass materials either virgin in nature such as trees, crops and vegetation or as waste such as refuse-derived fuel (RDF) represent an energy source much like conventional fuels. They vary in composition, density, heating value and other properties. Recycling them as industrial fuel has the added advantage of minimizing the severe and continuing problems associated with solid waste disposal. The total estimated quantity of organic wastes generated in 1980 (9) in the U.S. was about 1 trillion kilograms (1150 million tons). Approximately 15 percent is potentially recoverable and assuming a typical heating value of 2780 gcal/gm (5000 Btu/lb), this energy displacement might be equivalent to 1.2×10^{18} Joules per year or 1.1 quads per year (500,000 bbl oil equivalent per day) when converted to useful fuels.

There are two fundamental methods of biomass conversion to clean fuels: thermochemical and biochemical conversion. While the latter route is the most prevalent currently in development, processes that can produce petroleum-like synthetic fuels should be more desirable than alcohol fuels for example, in that they do not require significant modifications to the existing nationwide network of refining, transporting and utilizing liquid hydrocarbon fuels. Furthermore, because of the unique composition of biomass relative to that of petroleum, selective biomass conversion may result in the generation of high valued, specialty fuels such as certain phenolic compounds having high octane values.

The thermochemical route also has the following potential advantages over that of the biochemical route:

- o Higher thermal efficiency;
- o Wider applicability to feeds containing lignins and contaminants (e.g., MSW);
- o Production of completely detoxified products;
- o Access and similarity to the advanced state-of-the-art technologies utilized in the petroleum/petrochemical/coal industries.

The latter feature is the basis for applying the ITSL co-processing flowscheme to the utilization of biomass feedstocks. The economic driving forces delineated previously for the case of Devonian shale co-processing are even more profound for biomass applications, in particular, the organic-rich fraction of municipal solid waste (sometimes referred to as refuse-derived fuel-RDF). In a manner similar to that previously described for the case of Devonian shale co-processing, it can be shown that it may be feasible to justify the economic tradeoff between the differential values of petroleum feedstocks and MSW tipping fees.

However, because of the smaller capacities associated with MSW collection and classification, co-processing of petroleum residua and liquids derived from RDF would probably be limited to refinery hydrotreaters having capacities below about $3.18E6$ L/day (20,000 bbl/day). Furthermore, lower feedstock ratios of biomass-derived liquids to those of the petroleum liquids would be necessitated because of the availability and current design capacity of typical MSW classification units. This would in turn result in the co-processed liquids being more petroleum-like and thereby posing less potential problems to the refiner. A similar analysis can be performed of the co-processing of petroleum residua with wood chips derived from forest wastes.

Some preliminary screening tests were made in the batch autoclave reactor systems, similar to those made with the Devonian oil shale samples, utilizing two biomass feedstocks: pine wood flour and dust RDF. The results of these tests and the feedstock properties will be discussed at the Symposium.

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FIGURE 1
ALTERNATIVE CO-PROCESSING FLOWScheme FOR COAL AND HYDROTREATED RESIDUA

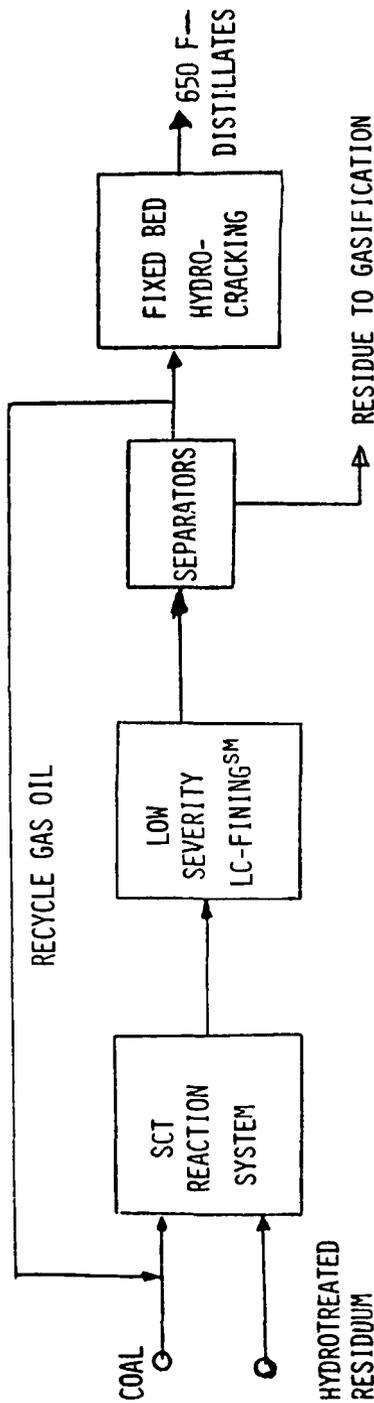
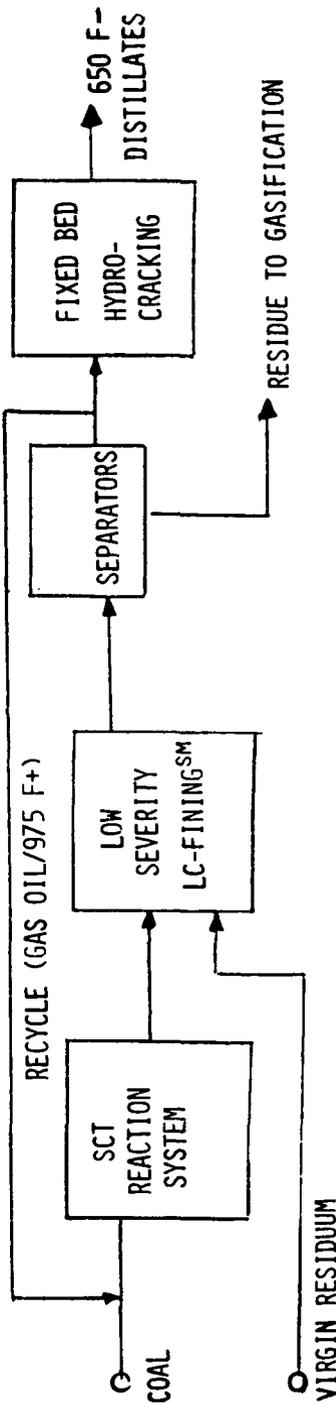


FIGURE 2
ALTERNATIVE CO-PROCESSING FLOWScheme FOR COAL AND VIRGIN RESIDUA



COPROCESSING OF HIGHVALE COAL WITH ATHABASCA BITUMEN IN SYNGAS MIXTURES,

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ABSTRACT

Coprocessing of Alberta subbituminous coal with bitumen is currently under investigation at the Alberta Research Council. The high oxygen content of the coal results in high hydrogen consumption. The present study compares the effectiveness of syngas/water mixtures catalyzed by potassium carbonate for coprocessing Highvale coal with Athabasca bitumen. Single-stage (solubilization) experiments were performed with syngas (5.1 MPa) at 390°C in a stirred autoclave. In simulated two-stage experiments, the second (upgrading) stage employed hydrogen (8.5 MPa) at 440°C with a potassium molybdate/dimethyldisulfide catalyst.

Coal conversion improved from 47 to 78% systematically when the carbon monoxide: hydrogen ratio was varied from 1:3 to 7:1. The additional yield was confined to pyridine extractable material. In simulated two-stage experiments similar coal conversions were observed when using carbon monoxide/water (91%) or hydrogen (88%) in the first stage.

INTRODUCTION

Within the Province of Alberta there are vast proven reserves of hydrocarbons in the form of coal ($2780 \cdot 10^9$ tons), heavy oil and bitumen ($200 \cdot 10^9$ m³) and natural gas. The subbituminous coal is mined from shallow deposits and used locally for the thermal generation of power. Bitumen is also surface mined as oil sands; extracted on site and upgraded to a synthetic crude oil ($20 \cdot 10^3$ m³/day) in two commercial operations. Heavy oil is mostly recovered by thermal processes from deeper deposits. It is used in the production of asphalt or blended with light crudes to produce a refinery feedstock.

The low cost of the mined coal (US \$12/ton) has provided the impetus to investigate processes^{1,2} to convert the coal into more valuable hydrocarbon products. Recent studies^{1,2} at the Alberta Research Council (ARC) have indicated that the coprocessing of Alberta coal with bitumen or heavy oil is technically and economically superior to direct coal liquefaction. Coprocessing eliminates the need for recycle solvents and takes advantage of synergistic effects to improve the liquid yields and product quality from the two feed components.

Laboratory and bench unit studies have shown that two-stage coprocessing has distinct advantages over a single stage operation. Lower temperatures can be employed during the first stage which permit solubilization of the coal while minimizing coke and gas production. The second stage operates at cracking temperatures 430-460°C, conditions which favour upgrading of both the coal and bitumen to liquid products.

Both stages require the use of hydrogen at moderately high pressures (16 MPa). The high oxygen content of the low rank coal means that excessive quantities of expensive hydrogen are needed to convert the oxygen to water, in addition to hydrogen uptake by the coal and bitumen. Although Alberta presently has ample supplies of natural gas for this purpose.

Earlier work^{3,4,5} has proven that CO/H₂O is more efficient than hydrogen at solubilization of coal in bitumen at temperatures below 400°C. More coal is dissolved and the reaction proceeds much more rapidly. The water gas shift reaction does not go to completeness during coal liquefaction or coprocessing. Equilibrium concentrations of carbon monoxide may exceed 50% with the bulk of the remaining gases being carbon dioxide and hydrogen. In a commercial operation it would be necessary to remove the carbon dioxide and recycle the unconverted carbon monoxide and any produced hydrogen. This present study was carried out to compare the efficiency of carbon monoxide/hydrogen mixtures with pure carbon monoxide for the solubilization of coal in bitumen and to establish the maximum permitted limit of hydrogen in the recycle gas steam. In addition, simulated two-stage experiments allowed a comparison of carbon monoxide and hydrogen in the overall coprocessing operation.

EXPERIMENTAL

Coprocessing experiments have been performed at ARC in miniautoclaves, 1 litre batch autoclaves, a hot charge-discharge unit and a 2 litre/hour bench unit. Since this work was restricted to the batch autoclaves, a brief description of the procedures will be given. Two modes of operation were employed: single stage and simulated two-stage.

In the single stage process coal, bitumen and an aqueous solution of potassium carbonate (shift reaction catalyst) were loaded into the autoclave. The autoclave was charged to 5.2 MPa (750 psi) with the gas mixture and heated to run temperature at about 5°C/minute. Operating conditions are listed in Table 1. When the run was complete the reaction mixture was cooled rapidly to 350°C by passing water through an internal cooling coil. The gaseous components were discharged at this elevated temperature through a condenser immersed in ice water. Gas volume was measured by a dry gas meter and its composition was determined by gas chromatography. The hot discharge eliminated foaming problems, due to dissolved carbon dioxide, which occurred when the unit was depressurized at room temperature.

In the simulated two-stage mode the process initially duplicated the single stage operation. Upon completion of the first stage a cracking catalyst, potassium molybdate/dimethyldisulfide (DMDS), was injected into the autoclave through a port in the head. The unit was repressurized with hydrogen 8.6 MPa (1250 psi) and a second heating cycle was completed. As before the gases were discharged at 350°C. The condensed oils and water from the two stages were combined prior to product distillation while the gas samples were analyzed individually.

A standard laboratory product separation procedure was established (Figure 1) to give distillable oil yield to 525°C, pyridine soluble organic material and insoluble organic material (IOM) remaining in the ash. Coal conversion was defined as $\frac{\text{Input coal} - \text{IOM}}{\text{Input coal}} \times 100\%$.

Properties of Highvale coal and Athabasca bitumen are given in Table 2. Both single and simulated two-stage experiments were performed in duplicate.

RESULTS AND DISCUSSION

A. Single Stage Experiments

Coal conversion and product distribution are summarized in Table 3 and Figure 2. The coal conversion can be seen to decline as the carbon monoxide content of the initial gas mixture was reduced. The pure carbon monoxide was much superior to the pure hydrogen while 50% carbon monoxide was still equal to the latter. These results ignore any pressure effects. Run pressure was lower at the lower carbon monoxide concentrations since the initial pressure was fixed. However, the partial pressure of the more active gas, carbon monoxide, was not constant. The initial pressure in the pure hydrogen run was 8.2 MPa (1200 psi) which could explain why it gave better coal conversion than 25% carbon monoxide.

Little evidence of upgrading of the coal or bitumen was observed apart from coal solubilization. Hydrocarbon gas and distillable oil yields were constant suggesting that thermal rather than chemical effects were responsible for their production. The distillable oil yield was essentially unchanged from that derived from the bitumen in the feedstock (33%); ie 525+°C conversion was zero. The only measurable change occurred in the formation of pyridine soluble organics, where pure carbon monoxide was most effective. Pyridine solubles declined in parallel with the coal conversion at the lower carbon monoxide concentrations. This confirmed earlier work that showed carbon monoxide was more effective than hydrogen for the solubilization of coal below 400°C due to the increased reactivity of the reducing species produced by the shift reaction, compared with molecular hydrogen.

Carbon monoxide conversion to carbon dioxide and hydrogen, varied little, being 61 ±1% for all experiments except the 25% carbon monoxide run (Table 4). As expected carbon dioxide production exceeded that of hydrogen in all cases although they should be equimolar if both were derived solely from the shift reaction. The coal had a high oxygen content, part of which is converted thermolytically to carbon dioxide upon heating. Produced hydrogen was below that expected from the shift reaction plus that initially present; consumption ranged from .4 to .7 moles per 100g of feed with a suggestion of a downward trend at lower carbon monoxide concentrations.

Hydrogen sulphide production was relatively constant at 0.2% MAF feedstock except for the pure hydrogen run where the higher partial pressure of reducing gas may have contributed to giving a slightly higher value, 0.3%. Thermal effects again appeared to outway chemical effects.

Product quality, expressed as elemental analyses was independant of the reducing gas composition. Hydrogen to carbon ratios were 1.6 for the distillable oils and 1.25-1.35 for the pyridine extract, sulfur was 2.6-2.8% and 3.4-4.1% respectively. Approximately 10% of the sulfur in the feedstock was converted to hydrogen sulfide, while little or none was present in the insoluble organic matter and ash. The majority of the input sulfur (96%) was derived from the bitumen and it remained within those fractions where the

bitumen products were concentrated, ie. the distillable oil and pyridine solubles. Little or no upgrading in terms of heteroatom removal could be attributed to the carbon monoxide solubilization process.

Simulated distillations of the distillable oils showed little variation (Table 5). The naphtha fraction accounted for $\approx 10\%$ while the medium oil fraction was $\approx 55\%$. Class analyses of the pyridine extracts, ie. non-volatile hydrocarbon, asphaltenes and preasphaltenes gave interesting results. The hydrocarbon content decreased as a percentage of the pyridine solubles as the carbon monoxide increased but the mass was relatively constant. Asphaltenes increased both in percentage and absolute terms. This suggested that the hydrocarbons required lower operating severity (less carbon monoxide) to solubilize, increased severity would result in more asphaltenes in the pyridine extract. More experimentation is required to confirm this observation because of the high scatter in the data.

B. Two Stage Experiments

Gas composition and conversion were discussed for the first stage in the previous section. Consumption of hydrogen in the second stage was not altered by the reducing gas used in the first stage. Hydrogen sulfide and hydrocarbon gas production were also constant, once more the result of thermolytic reaction pathways (Table 6). The difference in carbon oxides was quite marked, a factor of 10 greater for the carbon monoxide and 3 for the carbon dioxide in the carbon monoxide runs. It is most likely that these gases remained dissolved in the bitumen/coal liquids when the autoclave was vented at 350°C and were subsequently released in the second stage.

Product yields and distribution (Table 7) were not altered by the nature of the reducing gas present in the first stage. Overall coal conversion improved to approximately 90%. A high degree of upgrading took place with no difference attributable to the improved coal solubilization found in the carbon monoxide first stage. Pyridine extractable material declined from almost 60% to 22% of the product. Most of this material was converted to distillable oils. The hydrocarbon gas yield was high, combined first and second stage gas production being 10%. Conversion of the 525+°C material was 63% in both experimental modes.

CONCLUSIONS

Carbon monoxide was superior to hydrogen for the solubilization of coal in bitumen at temperatures below 400°C. However, it provided no benefit in a two stage process in terms of coal conversion, 525+°C conversion, and product quality. It does offer some potential economic benefits since lower temperatures can be employed in the first stage.

Coal solubilization could still approach 80% if the carbon monoxide stream contained hydrogen. Up to 25% hydrogen could be tolerated before a significant reduction in solubilization was observed. If the syngas mixtures function as rapidly as the pure carbon monoxide, then process improvements over pure hydrogen would include reduced first stage residence time and thus a smaller reaction vessel.

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Table 1
Operating Conditions

	1st Stage	2nd Stage
Gas	CO/H ₂ or H ₂	H ₂
Pressure (MPa)	5.2 or 8.2	8.5
initial reaction	15.6-20.7	15.3-19.0
Temperature (°C)	390	440
Reaction time (min.)	30	60
Feed	Highvale Coal/ Athabasca Bitumen	non distillables from Stage I
Ratio	1:2.5	-
Catalyst	K ₂ CO ₃	K ₂ MoO ₄ /DMDS

Table 2
Properties of Feedstocks

	Highvale Coal	Athabasca Bitumen
Moisture	6.4%	-
Ash (as is)	13.5	-
Carbon	75.0	82.0%
Hydrogen	4.3	10.6
Nitrogen	1.1	0.6
Sulphur	0.2	4.5
Oxygen ¹	19.3	2.3
Distillables (525°C)	N/A	46
Pyridine Solubles	N/A	54
Hydrocarbons	-	29
Resins	-	48
Asphaltenes	-	23

¹ by difference

Table 3
Coal Conversion and Product Distribution -
Single Stage Experiments

Carbon Monoxide Concentration (%)	100	87	75	50	25	0 ¹
Coal Conversion (% MAF coal)	85	76	75	65	47	65
Product Distribution(g/100 g MAF feed)						
Hydrocarbon gases (C ₁ -C ₅)	1	1	1	1	1	1
Distillable Oils (up to 525°C)	31	32	32	32	32	31
Pyridine Soluble Organics	57	54	51	50	47	53

¹ Initial pressure 8.2 MPa (1200 psi)

Table 4
Gas Production and Consumption

Carbon Monoxide Content	100 ¹	87	75	50	25	0 ¹
CO conversion %	62	63	60	62	44	-
Gas Production (moles)						
Carbon dioxide	1.26	1.06	1.00	.62	.36	.11
Carbon monoxide	-.97	-.86	-.67	-.49	-.18	-
Hydrogen	.52	.56	.48	.46	.36	-.25
Hydrogen Sulfide	.013	.011	.009	.009	.009	.017

¹ from 1st stage of 2 stage experiments

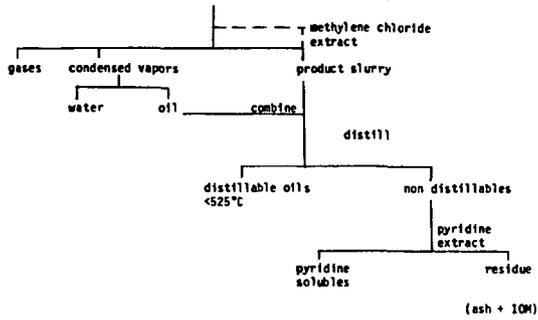
Table 5
Product Qualities - Single Stage Experiments

Carbon Monoxide %	100 ¹	87	75	50	25
A. Distillable Oil ²					
Naphtha		9	7	10 ¹	11 ¹
light gas oil		55	54	58	60
heavy gas oil		36	39	32	29
sulfur	2.6	2.6	2.7	2.7	2.8
hydrogen:carbon	1.65	1.6	1.6	1.6	1.6
B. Pyridine Extract					
hydrogen:carbon	1.35	1.3	1.25	1.25	1.25
nitrogen	2.3	1.6	1.2	1.1	1.3
sulfur	3.4	3.8	4.1	3.7	4.0
C. Class Analysis					
hydrocarbons		49	45	61 ¹	60
asphaltenes		43	50	31	31
preasphaltenes		8	5	7	9

¹ single analysis

² all percent except hydrogen to carbon ratio

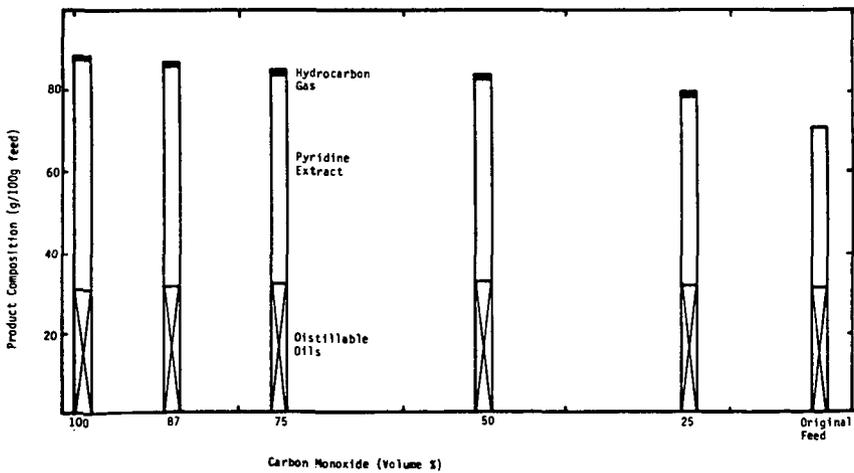
Figure 1
Product Work-up Procedure



Analysis performed

gases	:	composition, C ₁ -C ₅
water	:	none
distillable oils:		C, H, N, S, simulated distillation
pyridine extract:		C, H, N, S, class analysis
residue	:	proximate

Figure 2: Coprocessing Product Yields as a Function of Reducing Gas Composition



RECENT DEVELOPMENTS IN TWO-STAGE COAL LIQUEFACTION AT WILSONVILLE,

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INTRODUCTION

This paper will present results from the Advanced Coal Liquefaction R&D Facility at Wilsonville, Alabama. The primary sponsors are the U.S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI). Amoco Corporation became a sponsor in 1984 through an agreement with EPRI. The facility is operated by Catalytic, Inc., under the management of Southern Company Services, Inc.

RUN 247

Run 247 employed Illinois No. 6 coal in a configuration called the Reconfigured Integrated Two-Stage Liquefaction (RITSL) mode (Figure 1). Coal is slurried with a recycled process solvent and fed to the dissolver under hydrogen pressure where thermal liquefaction takes place. Thermal distillate is separated by fractionation, and the vacuum bottoms along with a heavy fraction of distillate make up the feed to the hydrotreater. This hydrotreater feed containing the thermal resid, unconverted coal, and ash is fed directly to the ebullated bed hydrotreater. The vacuum-flashed bottoms from the hydrotreater is the feed to the Critical Solvent Deashing (CSD) unit. The recycle solvent is composed of the deashed hydrotreater resid (HR) and hydrotreated distillate solvent.

Prior to Run 247, most runs had used the Integrated Two-Stage Liquefaction (ITSL) configuration, as illustrated in Figure 2. In the ITSL mode, the vacuum resid from the thermal liquefaction stage is deashed in the CSD unit before being fed to the hydrotreater.

Operation in the RITSL configuration was a step in the program to operate with close-coupled reactors, where the products from the liquefaction stage would be fed directly to the hydrotreater without any intermediate ash or distillate separation.

Because the hydrotreater feed was not deashed, it contained all the coal ash along with unconverted coal and heavy organics that would normally be removed in the deashing step. Thus, there was concern that the catalyst deactivation rate would increase. Another operability question concerned the effect of the RITSL mode on deashing. Since the feed to the CSD unit would be the vacuum-flashed bottoms from the hydrotreater, the CSD feed properties were expected to be different from feed properties that had previously been experienced.

Run 247 Results

The hydrotreater catalyst performed well in the RITSL mode. The catalyst used for all the runs in this report was Shell 324-M, a unimodal Ni-Mo catalyst. Throughout the run, catalyst activity measured by resid conversion was higher than in previous runs in

the ITSL configuration. This catalyst was aged to 1225 lbs (resid + UC + ash)/lb catalyst. The nondeashed feed did not cause serious deactivation of the catalyst (1).

Operability of the CSD unit with hydrotreated feed was satisfactory. The CSD feed did have different properties than feeds in the ITSL mode, but process adjustments were made which provided good deashing performance.

Representative Run 247 results in the RITSL mode are compared to a previous ITSL run in Table 1. The second column (243JK/244B) lists ITSL data that compare closely in operating conditions and cover a similar range of batch catalyst age as the RITSL data (247D). The RITSL distillate yield was 62%, compared to 59%. However, the distillate yields combined with the resid yields indicate that both configurations would have total liquid yields of 65% with zero resid.

A major difference is that the hydrogen consumption was 1% higher with RITSL, so the hydrogen efficiency was lower. The higher hydrogen consumption with RITSL is thought to be primarily related to higher resid reactivity. This improved hydrogenation activity is apparently caused by differences in the feed hydrocarbons or the presence of coal ash particles or both.

Run 247 Product Quality

Product blends were made by mixing product streams in the proportions of their production rates. These blends were then fractionated into boiling point cuts and elemental analyses were made of the individual fractions. Table 2 shows the product analyses for a Run 247 sample compared to a Run 244 sample to enable a direct comparison of products produced in the RITSL and ITSL configurations. The hydrogen contents of comparable fractions is higher, by 0.8-1.2%, for RITSL. The H/C ratios are higher by 0.10-0.16. In general, the RITSL product had lower levels of nitrogen and sulfur. These results appear to be evidence of increased hydrogenation. Therefore, the higher hydrogen consumption seems to be a trade off with improved product quality.

Mixing Study

A mixing study was conducted to quantify the degree of mixing in the dissolver. Mixing was studied by using radioactive tracer tests. The residence time distributions were fitted by a simple model. Importantly, the dissolver was found to be well mixed (3).

RUN 248

The configuration used at the beginning of Run 248 was the Double-Integrated Two-Stage Liquefaction (DITSL) mode, which is shown in Figure 3. This differs from the ITSL mode in that only the Light Thermal Resid (LTR) is routed through the hydrotreater. The heavier Thermal Resid (TR) is recycled directly to the thermal first stage. A potential advantage of the DITSL configuration is that a smaller hydrotreater might be possible because only the LTR stream is hydrotreated (2).

In the DITSL configuration, the heavy thermal resid is recycled to the liquefaction stage without going through the hydrotreater. Thus, the TR must be converted in the thermal stage for the DITSL mode to be viable. Iron oxide was used to promote resid conversion (4). Dimethyl Disulfide (DMDS) was added to the coal slurry to provide a source of hydrogen sulfide to convert the iron oxide to pyrrhotite as the slurry flowed through the preheater. This was the same method that was used successfully in Run 246 (2).

Before beginning the run, the 12-inch diameter dissolver was replaced by a 5.2-inch diameter Low Contact Time (LCT) dissolver. This was done to allow operation at lower liquefaction reactor volumes than could be achieved with the 12-inch dissolver. The intent was to investigate reaction times somewhat longer than had been used in the Short Contact Time (SCT) tests in Run 242 (5).

Run 248 Results

Operation in the DITSL configuration was difficult. The major operability problem was high viscosities of the TR, the process solvent, and the coal slurry. The recycle of the heavy TR directly from the CSD unit resulted in a buildup of preasphaltenes, which caused the high viscosities. Process variable adjustments were made in an attempt to achieve viable operations in the DITSL mode. The dissolver outlet temperature was raised to 840°F to increase the severity for resid conversion. However, resid conversion in the thermal unit was not sufficient to allow satisfactory operation in the DITSL configuration.

Satisfactory operability was obtained by changing to the ITSL configuration. The distillate yield was 64% and the resid make was 3%, for a total liquid yield of 67% (248D). This compares favorably to the 65% yields shown earlier for the RITSL and ITSL configurations with Illinois No. 6 coal. Because of other process variable differences, most notably dissolver temperature, it can not be concluded from these results if iron oxide caused an improvement in distillate yield.

The addition of iron oxide and DMDS was stopped, to begin a series of tests at different reactor volumes. After a three-day test at 100% LCT without iron oxide, the dissolver volume was reduced successively to 50% and then to 25% LCT dissolver volume. Coal conversions with volumes of 100%, 50%, and 25% were 92%, 90%, and 88% MAF coal, respectively. As expected for the reduced contact times, resid makes increased and distillate makes and hydrogen consumptions decreased.

Conditions and two-stage liquefaction (TSL) yields for the 50% LCT period (248F) are compared to Run 242 SCT results in Table 1. Coal space velocities using the reaction volume above 700°F were comparable for these two conditions. The yields were very similar, though SCT showed an advantage in lower gas make and hydrogen consumption. A close examination of conditions indicated that the average reaction temperature was higher for 248F.

Run 248 Product Quality

Properties of a fractionated product blend from period 248D (ITSL with iron oxide) are shown in Table 3. As can be seen, the product boiling below 650°F is 67% of the total blend, which is comparable to that obtained in Run 244 without iron oxide (Table 2).

The naphtha from 248D had higher hydrogen content (13.76 vs 12.86) but the nitrogen and sulfur were higher. The analyses for the distillate and gas oil fractions were similar, with 248D showing slightly higher nitrogen and sulfur contents. The API gravities showed that the naphtha and distillate for 248D were heavier than those from Run 244.

RUN 249

A major objective was to obtain process yield data using subbituminous coal with a well-mixed dissolver. A pumparound loop was installed to provide back mixing of the 12-inch dissolver.

The RITSL configuration was used to provide a data base for predicting process performance with subbituminous coal in a close-coupled configuration.

Two additives were investigated for enhancement of conversion of the subbituminous coal. The effectiveness of iron oxide with DMDS had been demonstrated earlier (2). Work at the University of Wyoming had shown some very interesting results related to coal drying and the use of water in liquefaction of subbituminous coal (6). Coal conversions were improved when coal was not completely dried or even when water was added back to a coal slurry of dried coal before liquefaction. The water effect was found to be additive to the iron oxide effect on coal conversion. The effect of water addition was tested by adding water at the rate of 15% MF coal to the coal feed slurry.

Run 249 Results

The run was started with the dissolver at 790°F and the hydro-treater at 670°F and with no iron oxide or water addition. The coal conversion was 82%. Coal conversion was increased to 90% by adding iron oxide plus DMDS and by increasing the dissolver temperature from 790 to 810°F. Water addition increased coal conversion by 3%. Iron oxide and DMDS addition were discontinued to test whether water addition without iron oxide could maintain coal conversion. Coal conversion decreased significantly, from 92 to 84%. Thus, water addback did not enhance coal conversion enough to enable operation without the iron oxide.

For the 1.5% iron oxide addition rate, the coal sulfur content was calculated to be sufficient to convert the iron oxide to pyrrhotite. This was tested by stopping the DMDS addition and no reduction in coal conversion was observed. Therefore, iron oxide was used without the addition of DMDS for the last two months of the run.

Energy rejection was high throughout this run because the CSD feed was very soluble and the solubility changed with various operating variable adjustments. Energy rejection was reduced by changing solvent type and adjusting operating conditions. The CSD experience gained in this run will be valuable in processing the highly soluble feeds that are expected to be encountered in the close-coupled operations.

Selected process conditions and yields for Run 249 are shown in Table 1. The only difference in periods 249D and 249E is that water addback was used in 249D.

The negative resid make for 249E indicates that more resid was being converted than was being made, so that resid was being consumed from inventory. The C₄+ distillate yield for 249E would be about 53% if the resid make had been zero. Thus, there was practically no effect of water adback on distillate yield for this comparison.

The last major period of the run, designated 249H, was an ash recycle test. The purpose of this test was to remove ash from the system by using a purge of hydrotreater vacuum bottoms instead of using the CSD unit. The ash content of the purge stream was increased by recycling a portion of the hydrotreater atmospheric flashed bottoms to the dissolver. This recycled solvent contained ash, iron oxide, unconverted coal and hydro-treated resid and distillate. By using this method, the solids content of the vacuum bottoms purge stream was increased to about 50% unconverted coal and ash. The ash content was 32%.

The recycle test resulted in significantly increased coal conversion. The 94% coal conversion obtained in period 249H is the highest obtained with subbituminous coal at Wilsonville. It is notable that this high conversion was obtained with a moderate dissolver temperature of 802°F. The increased coal conversion was probably due to additional conversion of the unconverted coal in the recycle stream. The recycled ash and iron oxide also probably contributed to enhanced reactivity.

The yield results are similar to 249E, but the hydrogen consumption was higher. These results were encouraging and suggest that a vacuum tower could be used as an alternate method of removing ash from the system.

A comparison of data for 249E and 2496G in Table 1 provides a comparison of the RITSL and ITSL results with subbituminous coal. A number of differences are apparent in the operating conditions. In particular, Run 249E had a lower dissolver temperature and a considerably higher hydrotreater temperature. Also, 249E had a forced back-mixed dissolver while 2496G did not. Surprisingly, the yields are fairly similar. As a result of the lower dissolver temperature, 249E had a lower gas make. The sum of distillate and resid is comparable for the two periods. Several factors may have contributed to the higher hydrogen consumption of 249E, but the RITSL configuration is probably the main reason.

An analysis of catalyst behavior in Run 249 has not been completed. However, the catalyst performed adequately throughout the run and a catalyst age of 1870 lb (resid + UC + ash)/lb was reached. The catalyst used for Run 249 was the Shell 324-M catalyst used in Run 246, with an initial age of 617. Catalyst deactivation was observed during the run, but the resid conversion activity appeared to be relatively constant over the last half of the run.

1985 ACCOMPLISHMENTS

The RITSL configuration was demonstrated for both bituminous and subbituminous coals and the results were positive. These runs provide a solid basis for close coupling the reactors. A very successful mixing study was performed to quantify the degree of

mixing in the thermal reactor. Iron oxide and water were tested as disposable catalysts. Iron oxide has been tested in both the ITSL and DITSL configurations with both coals. The experience with increased CSD feed solubility broadened the knowledge of CSD operations. This will be applicable in the close-coupled runs. Lastly, an alternate method of removing ash from the system was demonstrated in the ash recycle test. This provides additional flexibility for future runs.

FUTURE WORK

The emphasis is on experimentation with close-coupled reactors. The Wilsonville plant has been modified by the addition of a reactor vessel adjacent to the hydrotreater to operate in a close-coupled fashion. The initial run will be a thermal-catalytic run, but the equipment is capable of operating with ebullated catalyst beds in both reactors. There are plans to test alternate catalysts.

The coal liquefaction data base will be expanded by parametric studies and by increasing efforts in the area of process modeling and simulation.

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TABLE 1
PROCESS CONDITIONS AND YIELDS

Run No. Configuration Coal	247D RITSL 111. 6	241JK/2448 ITSL 111. 6	248D ITSL 111. 6	248F ITSL 111. 6	242BC ITSL-BCT 111.6	249D RITSL 111. 6	249E RITSL Myo.	249H RITSL Myo.	249C ITSL Myo.
Thermal Stage	810	810	834	835	860*	796	796	802	813
Coal Space Velocity (lb/hr-ft ³ >700°F)	27	28	31	43	41	14	14	14	17
Solvent-to-coal Ratio	44.8	50.8	45.8	45.8	1.8	1.5	1.5	2.0	1.6
Steam (wt %)	44	50	45	45	46	30	29	22	30
Iron Oxide (% of HF Coal)	0	0	2.0	0	0	1.5	1.5	1.5	2.0
DMSO Addition	0	0	Year2	0	0	0	0	0	Year2
Catalytic Stage	710	720	785	728	720	700	700	700	625
Temperature (°F)	0-9	1.0	0-7	0.7	1.0	1.3	1.2	1.6	1.0
Space Velocity (lb feed/hr/lb cat)	51	55	57	57	55	35	34	27	54
Feed Resid Content (wt %)	445-670 ³	350-850	260-287	339-396	278-441	1119-1183 ³	1208-1246 ³	1683-1703 ³	496
Catalyst Age (lb resid/lb cat)									
Yield (lb H₂/lb Coal)⁴	6(12)	6(12)	8(13)	7(12)	4(9)	7(18)	6(14)	7(16)	9(19)
C-C ₃ Gas (Total Gas)	9	9	8	9	10	14	14	14	11
Water	9	9	8	9	10	14	14	14	11
C ₄ * Distillate	62	59	64	54	54	53	57	56	53
Resid	3	6	3	8	8	1	-4	-4	1
(Total Liquid Product)	(65)	(65)	(67)	(62)	(62)	(54)	(53)	(52)	(54)
Hydrogen Consumption	-6.1	-5.1	-5.6	-5.3	-4.9	-5.7	-5.8	-6.3	-5.4
Hydrogen Efficiency (lb C ₄ * Dist./ lb H ₂ Consumed)	10.2	11.5	11.3	10.2	11.0	9.3	9.9	8.9	9.8
Energy Rejected to Ash Conc. (%)	22	22	19	23	25	21	24	26	21

Inlet hydrogen partial pressure 2040 psi
³preheater outlet temperature. Dissolver was bypassed in Short Contact Time Run 242.
⁴Used LCV 5.2-inch diameter dissolver. Other runs used 12-inch diameter dissolver.
⁵Dimethyl Dianilide added at 1.1 x stoichiometric amount to convert Fe₂O₃ to FeS.
⁶Catalyst age for RITSL is lbresid + ash + unconverted coal/lb catalyst.
⁷Elementally balanced yield structures.

TABLE 2

properties of distillate product

sample: Wilsonville synthetic crude blend representative of TSL product slate

distillation cut	wt% of sample	elemental (wt%)					API gravity (60/60)
		C	H	N	S	O (diff)	
(A) run 244 (catalyst age ~ 1600 lbs resid/lb cat, HTR temp ~ 730 °F) ITSL configuration							
naphtha (IBP-360 °F)	18.4	85.21	12.86	845ppm	0.36	1.50	43.1
distillate (360 °F-650 °F)	45.7	86.34	10.73	0.23	0.22	2.48	18.6
gas oil (650 °F-1000 °F)	35.0	89.07	9.69	0.31	0.16	0.76	7.3
resid (1000 °F+)	0.9	86.71	6.94	1.13	0.60	3.15	—
(B) run 247 (catalyst age ~ 283-372 (lbs resid + UC + ash)/lb cat, HTR temp ~ 700 °F) RITSL configuration (247C-II)							
naphtha (IBP-360 °F)	14.9	85.50	14.07	500ppm	0.35	0.03	—
distillate (360 °F-650 °F)	49.8	86.74	11.54	0.23	0.16	1.33	—
gas oil (650 °F +)	35.3	89.48	10.44	0.06	0.02	0.00	—

*work performed by Amoco Oil Company

TABLE 3

properties of distillate product

sample: Wilsonville synthetic crude blend representative of TSL product slate

distillation cut	wt% of sample	elemental (wt%)					API gravity (60/60)
		C	H	N	S	O (diff)	
(A) run 248 (catalyst age ~ 300 lbs resid/lb cat, HTR temp ~ 700 °F) ITSL configuration (248D)							
naphtha (IBP-350 °F)	18.6	84.63	13.78	0.13	0.65	0.83	42.4
distillate (350 °F-650 °F)	48.1	84.45	10.94	0.23	0.37	4.01	13.2
gas oil (650 °F+)	33.3	89.11	9.41	0.43	0.18	0.87	0.3
total blend	100.0	85.72	10.78	0.22	0.42	2.86	14.1

**two-stage liquefaction
reconfigured mode (RITSL)**

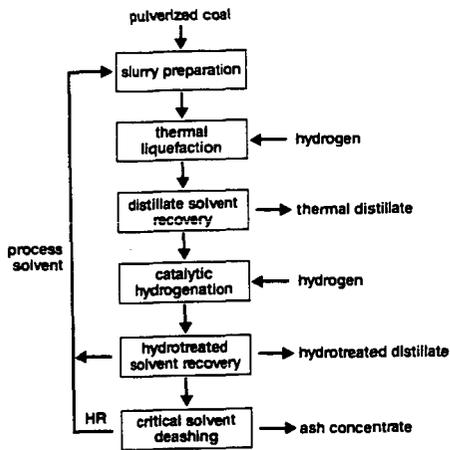


FIGURE 1

**two-stage liquefaction
integrated mode (ITSL)**

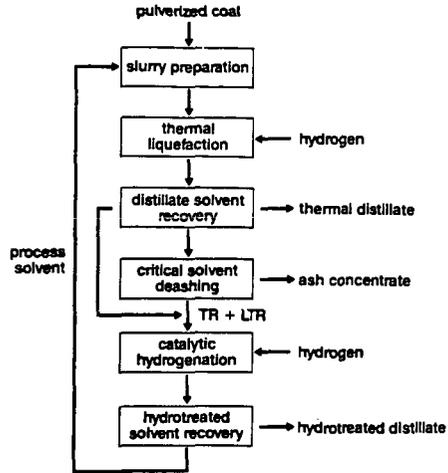


FIGURE 2

**two-stage liquefaction
double-integrated mode (DITSL)**

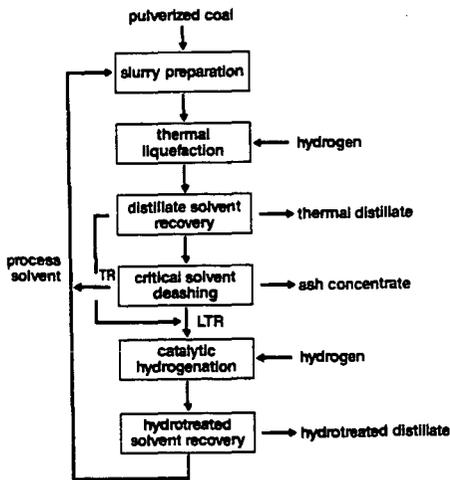


FIGURE 3

REFINING COAL LIQUIDS: WHERE WE STAND

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ABSTRACT

In extensive studies sponsored by the US Department of Energy, syncrudes from a variety of coals (bituminous, sub-bituminous, lignite) and several direct coal-liquefaction processes (SRC-II, H-Coal, EDS, ITSL) were catalytically hydroprocessed in pilot plant tests. The results show that these syncrudes can be refined to transportation fuels (diesel, jet fuel, gasoline) using commercial petroleum hydroprocessing technology. Key factors that determine how easy or difficult a particular syncrude is to refine are boiling range (endpoint), hydrogen content, and heteroatom content. This paper reviews experimental results, discusses alternative refining routes, compares projected costs for these routes with different feeds, and identifies areas in which further research is needed.

INTRODUCTION

The name "syncrude" or "synthetic crude" is used rather loosely to describe hydrocarbon oils derived from sources other than petroleum. The name implies that they can serve as substitutes for petroleum crude. However, liquids produced from coal in direct-liquefaction processes are quite different from petroleum. Can they really take the place of petroleum? Can we make products from coal syncrudes that meet petroleum specifications using conventional refining technology? If so, are there differences between products from petroleum and those from coal-derived oils? Are fuels from coal better or worse than conventional petroleum-derived fuels? How much will it cost to refine coal syncrudes?

For several years, Chevron under a contract with the US Department of Energy has been studying the refining of coal liquids. Detailed results are given in a series of DOE Interim Reports (1). This paper briefly reviews that work. Also, we will address the above questions, and identify areas in which further research is needed. For a more extensive overview of the state-of-the-art in coal liquids upgrading, the reader is referred to a recent comprehensive study by Oak Ridge National Laboratory (2).

DOE supplied to us the "net whole-liquid process product" from each of a group of liquefaction processes for which they have supported research and development. The processes are Solvent-Refined Coal (SRC-II), H-Coal, Exxon Donor Solvent (EDS), and Integrated Two-Stage Liquefaction (ITSL).

In our program, we developed conceptual refining schemes for processing each of the syncrudes in a "grass-roots" refinery (that is, a completely new stand-alone refinery) to produce fuels meeting current specifications. Then, we conducted pilot plant tests for the key upgrading steps to make reasonable estimates of commercial catalyst performance. Finally, detailed engineering studies were made to determine stock balances and estimate refining costs.

PROPERTIES OF COAL-DERIVED OILS

Table I summarizes some of the key properties of the coal-derived oils that served as feedstocks for our upgrading studies. For comparison, Arabian Light crude is also included. Each of the coal oils was selected by DOE to represent, as nearly as possible, the net whole-liquid product from the liquefaction process at the time it was chosen. However, it should be recognized that the properties may not be representative of the oil that an optimized commercial process would produce. All of the processes have only operated on a pilot plant scale; and none is yet fully optimized. Furthermore, each process can operate in various modes, generating products with different properties.

These oils differ from typical petroleum crudes in a number of ways: (1) They are generally much lower boiling than typical petroleum crude. (2) They contain no residuum. (3) They contain mostly condensed cyclic compounds and few paraffins. (4) Most have relatively high heteroatom contents, particularly nitrogen and oxygen. (5) Most have a relatively low hydrogen content compared to petroleum.

Figure 1 shows typical distillation curves of several coal-derived oils compared to typical Middle-East petroleum crudes. (The curves for the H-Coal oils are not shown in the figure, but fall into the envelope included by the other coal oils.) The coal oils contain little high boiling material compared to petroleum because most of the higher boiling oil is typically used as a recycle solvent in the liquefaction process and ultimately converted to lower boiling products. The boiling range of the oil used as solvent can vary, however, depending on how the liquefaction process is operated. Therefore, boiling range of the net product can also vary, and upgrading studies can help guide the selection of the best operating mode for the liquefaction facility.

There are some significant differences among the different coal liquids; particularly between the two-stage liquefaction product, ITSL oil, and the others. The ITSL oil contains a much larger middle distillate fraction (76 LV% boils between 400°F and 700°F) and less naphtha. It is also lower in heteroatom content and (except for SRC-II) lower in hydrogen content.

Some of the as-received oils, in particular the EDS and H-Coal oils shown in Table I, have appreciable quantities of a high endpoint "tail", which makes these stocks relatively hard to hydrotreat. We distilled these oils to remove the highest boiling fraction and hydrotreated the distillates as well as the whole oils. Properties of the re-distilled oils are also given in Table I.

In addition to the oils shown in Table I, we also studied the upgrading of several higher boiling coal oils. Results are given in DOE reports (1) and a recent paper (3). The heavy fractions of these oils could either be used as recycle solvent or be part of the net liquid product, depending on how the liquefaction process is operated.

CONCEPTUAL REFINING PLANS

We considered a variety of conceptual refining plans for orienting and guiding the pilot plant work. We will limit the discussion here to two basic plans and later use them as a framework for comparisons between the different coal-derived oils that were

processed. Simplified flow schemes for these refineries are shown in Figures 2 and 3. Each scheme represents the main hydrocarbon flow in a refining module, excluding the many supporting plants necessary in a full-scale "grass-roots" refinery, such as by-product recovery, waste treatment and hydrogen supply. Considering hydrocarbon flow alone, these coal liquid processing schemes are less complex than those required for a modern large petroleum refinery processing heavy crudes. This is because these coal liquids contain no residuum. But, whereas the flow scheme would be simpler than for petroleum, the processing would be at least as severe.

In the first refining plan (Figure 2), the target products are gasoline and middle distillates (diesel and/or jet fuel). Because most of the feed already boils in the range of the desired products, no cracking conversion process is required. The whole oil is hydrotreated at a high severity to produce specification jet fuel or diesel, and the naphtha is catalytically reformed to high octane gasoline. [This refinery could also produce No. 2 heating oil as the middle distillate product rather than jet/diesel. In that case, the hydrotreater could be operated at a lower severity than required for specification jet or diesel.]

In the second refining plan (Figure 3), as shown, the target product is all gasoline. In this case, as in the first refining scheme, the oil is first hydrotreated. However, the severity can be somewhat lower than in the first case, because the purpose is to remove heteroatoms rather than to make finished products. Then, the hydrotreated oil is hydrocracked to convert the high boiling fraction into naphtha, and the naphtha is then catalytically reformed to gasoline.

HYDROTREATING RUNS

As indicated earlier, full-boiling-range coal oils require relatively high hydrotreating severities to remove the heteroatoms and increase the hydrogen contents. Our hydrotreating studies have been described in detail elsewhere (1). Table II briefly compares results obtained with the feeds listed in Table I at comparable conditions with a single commercial hydrotreating catalyst, Chevron's ICR 106. The tests were made at 750°F average catalyst temperature, two hydrogen partial pressures (2300 and 1800 psia), and three different liquid hourly space velocities (LHSV): 0.5, 1.0, and 1.5 volumes of feed per volume of catalyst per hour.

The best direct comparison is at 1.5 LHSV and 2300 psia because all the feeds were tested at these conditions and the results show major differences. In Table II, the feeds are listed in order of ease of hydrotreating. The easiest feeds to upgrade are the redistilled Illinois H-Coal and lignite EDS, as indicated by the low product nitrogen and aromatic contents. Of the full-boiling-range oils, the Wyodak H-Coal is easiest, probably because of its high hydrogen content and low average boiling range.

ICR 106 catalyst was quite stable at 2300 psia for hydroprocessing all the feeds, except for the full-boiling-range lignite EDS oil. With the EDS oil, there was measurable decrease in hydrogenation activity with time on stream, even at 0.5 LHSV. We believe that this result was due to coke-precursors in the high endpoint "tail" of the EDS oil (Figure 1). When the high boiling

fraction was removed by distillation, the catalyst was very stable at these conditions.

At a lower pressure (1800 psia) and 1.5 LHSV, the catalyst was stable for both redistilled oils, and two of the full-boiling-range oils: Wyodak H-Coal and Illinois ITSL. However, in addition to the EDS oil, the Illinois H-Coal and the SRC-II oils also caused measurable catalyst deactivation at these conditions.

The hydrogen consumption needed for a given product quality from these coal liquids depends on their hydrogen content and heteroatom contents. It is higher than that usually needed in petroleum hydrotreating. Still, in spite of the relatively severe hydro-processing conditions, there was little cracking to light gases, and liquid-volume yields were typically higher than those obtained when hydrotreating petroleum (because of the higher hydrogen input).

We compared a series of oils produced in the ITSL process from two different coals--Illinois and Wyodak. These oils have different endpoints, and are not all full-boiling-range oils. However, Figure 4 shows a fairly good correlation between the required catalyst temperature for 0.5 ppm nitrogen product and the feed endpoint, regardless of coal source. With the oils with endpoints of 750°F or below, the catalyst is very stable, and catalyst lives of several years can be predicted at the test conditions. The higher temperatures required for hydrotreating the higher boiling feeds would significantly shorten the catalyst lives.

HYDROCRACKING RUNS

In a recent paper (4), we discussed in detail the hydrocracking of a representative coal oil, hydrotreated ITSL oil. Hydrocracking is a flexible process that can be varied to make only naphtha (as shown in Figure 3) or a combination of gasoline and middle distillate if the recycle cut point is increased. The products from hydrocracking coal oils are similar to those obtained from hydrotreating; the quantities of each can be varied depending upon the demand.

PRODUCT PROPERTIES

General Comments. After hydrotreating, products of similar boiling ranges from the different liquefaction processes and different coals are actually quite similar. After removal of the heteroatom-containing compounds, the products consist mainly of cyclic hydrocarbons. The severity of hydrotreating determines the amount of hydrogenation of aromatics to naphthenes. There are, however, some differences. Products from sub-bituminous coals contain more paraffins than those from bituminous coals, but fewer paraffins than products from lignites. Even so, the paraffin contents of lignite products are lower than petroleum products. For a given coal, ITSL process products contain fewer paraffins than those from the other processes. (Probably less ring opening occurs because of the lower severities required in two-stage liquefaction.)

Naphtha. Hydrotreated and hydrocracked naphthas from coal liquids are excellent feeds for catalytic reformers because of the high content of cyclic compounds. The naphthenes can be converted to high octane aromatics by reforming at relatively mild conditions. Also, because they are easy to reform, such naphthas can be reformed

at higher severities to an extremely high octane product, which makes a superb gasoline blending stock or which could be used for the production of benzene, toluene, and xylene as chemicals. Because of the mild conditions required to produce a given octane product compared to petroleum, much of the hydrogen previously consumed can be recovered (5).

Jet Fuel. To make jet fuel from these coal liquids, most of the aromatics must be saturated. To meet the smoke point specification of 20 mm or higher, the aromatic content for a full boiling range kerosene would typically be no higher than about 10 LV%.

Jet fuels prepared from coal liquids offer some unique advantages over those prepared from petroleum. They have unusually low freezing points (because of the low paraffin content). Also, because they contain high concentrations of naphthenes, they are very dense and have high heating values by volume. Therefore, they could have specialized uses such as for military fuels.

Franck et al (6) compared different hydrocarbon types to determine which had properties best suited for jet fuel. They showed that naphthenic hydrocarbons with two or three rings (molecular weight between 120 and 200) were the only ones to have all the following properties simultaneously: (1) high volumetric heat of combustion, (2) satisfactory mass heat of combustion, (3) acceptable thermal stability, (4) very low freezing point, (5) acceptable low temperature viscosity, (6) low volatility, and (7) acceptable flame characteristics. Because coal liquids are extremely rich in these compounds, they make high quality jet fuels.

Diesel Fuel. Diesel products from coal-derived oils also meet typical specifications including cetane number. As with jet fuel, most of the aromatics have to be hydrogenated before the specification for cetane number of 40 is met. With all the oils studied except ITSL oil, the aromatics content has to be about 10 LV% to meet this specification. With ITSL oils, the specification could be met with about 20 LV % aromatics present. The ITSL diesel had a somewhat higher average boiling range than the other diesels oils, and this may account for the difference.

Coal-derived liquids respond well to certain cetane improvers. Because of the high cost of hydrogen, it may be cost effective to substitute cetane improvers for hydrotreating severity to some extent. For example, adding 0.3 LV% octyl nitrate (a commercial cetane improver) to diesel fuels from hydrotreated Wyodak H-Coal oil was shown to increase the cetane number by 6-8 numbers (7).

As with jet fuel, the diesel fuels also have excellent cold weather properties, and high volumetric energy contents.

Heating Fuel. Although the primary purpose of our studies is to make transportation fuels, we have also evaluated No. 2 heating oil as a possible product. Generally, it is possible to make heating oil by hydrotreating coal liquids less severely than is necessary to produce jet and diesel fuels. All specifications can be met, except gravity. Probably, the gravity specification could be waived in some applications. (Usually, the gravity specification also can be met by hydrotreating at higher severity to make diesel-quality product.)

DETAILED REFINING PLANS AND STOCK BALANCES

Based closely on the results of the pilot plant work and conceptual refining plans, we developed detailed refining plans and stock balances for each coal-derived feedstock. The primary basis for the detailed plans and stock balances was to produce 50,000 barrels per calendar day of the desired products in a complete new refinery. This refinery would include all necessary supporting facilities such as utility plants, tankage, and required environmental control equipment. The refinery would be self-sufficient in fuel and hydrogen plant feed. It would produce finished distillate fuels meeting current specifications along with environmentally acceptable by-products, e. g., sulfur and ammonia.

Stock balances have two kinds of results: (1) individual plant capacities and (2) feed and product flow rates. Interested readers will find detailed comparisons of the stock balance results in the Tenth Interim Report listed in reference 1; only a brief summary is presented here. We used the stock balance plant capacities as part of the basis for the refining cost estimates. Stock balance flow rates are summarized as product yields along with the costs.

REFINING YIELDS AND COST ESTIMATES

Table III summarizes these results for the coal-derived oils studied by mid-1985. The costs are all given on a common basis, first quarter 1984 dollars. (Costs studies of ITSL oil upgrading are incomplete at the time of writing.) The oils are of two general classes: the "net whole-liquid process product" as received from DOE, and the stock as re-distilled at Chevron Research. There are three general refining modes as discussed above: two-stage hydrocracking to produce only motor gasoline, severe hydrotreating to produce motor gasoline and kerosene jet fuel or diesel, and less severe hydro-treating to produce motor gasoline and heating oil.

Because we assume "grass-roots", self-sufficient refineries for the comparison, the net yields allow for using part of the coal-derived feeds and/or refined products for hydrogen production and refinery fuel.

The investment costs are estimated from correlations of costs of actual petroleum processing plants built by Chevron over the last twenty years, adjusted for the many factors which have changed or could change if and when a synfuels refinery is constructed. The synfuels-specific plants (the hydrotreaters and hydrocrackers) are estimated in further detail; design conditions are based directly on the pilot plant data.

The histories of large, first-of-their-kind engineering projects show that the refining cost estimates will almost certainly change as synfuels development moves closer to commercialization. Therefore, the main value of the present estimates is not for predicting ultimate synfuels costs, but rather for comparing one set of results versus another--different feeds, different processing schemes, and different product mixes. The results, then, can guide future research and development. For this reason, we made a strong effort to keep the estimates consistent with each other.

From these refining costs, we can reach some qualitative conclusions. For example, the feeds rank differently depending on the product slate. To make all gasoline from the as-received stocks, the cost ranking is Pitt Seam SRC-II > Lignite EDS > Illinois H-Coal > Wyodak H-Coal. But the EDS stock would be the most expensive from which to make a combination of gasoline and jet fuel or diesel. Also, re-distilling affects the refining cost of each feed differently: \$4/BBL reduction for Lignite EDS, \$2.5/BBL for Illinois H-Coal, and no reduction for Wyodak H-Coal.

The refining yield and cost differences can be rationalized by considering the boiling range and composition of each feed: (a) higher boiling stocks are more expensive to refine but lend themselves to higher boiling products; (b) heteroatom content can influence refining cost, although it usually trends with boiling range; and (c) the cost difference between refining to gasoline and refining to jet and/or diesel fuel increases as the hydrogen content of the feedstock decreases. (For example, with high hydrogen-content feeds such as Wyodak H-Coal oil, the costs of making all gasoline or a combination of gasoline and jet/diesel are about the same. But with low hydrogen content feeds such as SRC-II, it is appreciably less expensive to make all gasoline than the combination.)

RELATIONSHIPS BETWEEN COAL-LIQUID AND PETROLEUM UPGRADING COSTS

Several facts must be kept in mind if one is to judge what these costs mean and how they might be applied in situations other than internal comparisons. First, with the present and quite probably the future excess of petroleum refining capacity in this country, no new "grass-roots" refineries are likely to be constructed for coal-derived oils. Instead, refining facilities either will be integrated with liquefaction plants, or even more likely, coal-derived stocks will be refined along with petroleum in existing refineries. Of course, refining costs will then be entirely different from those presented here. Second, petroleum refining costs themselves increased 50 to 60 percent between 1980--when we first published estimated costs of refining coal-derived oils--and 1984, the basis for the costs presented here. (They are estimated to have increased an additional 15% by the first quarter of 1986.) Correction factors must be applied to earlier cost studies, whether for coal-derived oils or petroleum. Finally, the size of the refinery affects per-barrel cost. For example, product from a 50,000 barrel-per-day refinery costs about 20% more than that from a 100,000 barrel-per-day refinery. [(1), Report 10].

As with coal liquids, the costs of refining petroleum vary widely, depending on boiling range, heteroatoms and metals contents, and desired product slate. Most petroleum crudes have the advantage of being relatively hydrogen-rich, but the disadvantage that they contain varying amounts of residuum.

There is little question that distillate fuels from coal will be more expensive than those from petroleum, based on the current prices of petroleum and state-of-the-art liquefaction and refining technologies (8). This is largely the result of the high cost of liquefaction, rather than the upgrading costs. We have not attempted to compare the costs reported here with those for upgrading petroleum. However, other studies --in particular, those of Universal Oil Products, Inc. (UOP) (9, 10, 11)--serve to put these costs in perspective.

For example, Sikonia et al (9) compared the costs of refining an H-Coal product and two petroleum crudes on an internally consistent basis. Overall refining costs were about the same--within 5% of each other. However, product slates were different--the coal oil was refined to gasoline and diesel, the petroleum crudes to a wider variety of products. In order to rank the feedstocks, the authors assumed a set of product values. Then, from these values, they calculated how much each feedstock was worth to the refiner. They concluded that the coal oil was worth about \$2/BBL more than Mexican Maya heavy oil, but about \$2.50/BBL less than Arabian Light crude oil. (It will, of course, be recognized that product values will change with time. Therefore, the ranking could change.)

In another study (10), Gembicki et al calculated costs for a conventional refinery, a heavy-oil refinery, and a coal-liquid refinery producing both gasoline and No. 2 heating oil. For that product slate, refining costs were greatest for the heavy oil refinery and least for the coal liquids refinery. The authors explained that the heavy oil required the largest conversion facilities, as it contained the least amount of distillables compared with the other feedstocks. The coal-liquids refinery was the least expensive because of the small quantity of residual matter found in the coal liquid. Nevertheless, they concluded that the entire cost of upgrading coal to distillate fuels would be much more expensive than upgrading heavy crude because of the high cost of coal liquefaction.

In an earlier analyses for DOE (11), UOP concluded that a refiner could afford to pay more for coal liquid than a Light/Heavy Arabian crude oil blend and still realize the same rate of return on investment for a new refinery specific to the feedstock processed. (Again, this applied to a specific product slate, and product values were assumed.) In this study, the small proportion of coal liquid feedstock boiling higher than the product endpoint was significant. If the proportion of such residue increased, the relative value of coal liquid would decrease due to the higher processing cost to convert heavy oil to lighter products.

CONCLUSIONS: WHERE WE STAND

If the properties of the coal liquids shown in Table I are indeed representative of the liquefaction products made from an eventual commercial process, there is virtually no doubt that they can be upgraded to specification transportation fuels using modern commercial petroleum-processing technology. Of course, not every refinery could handle them. High-pressure hydrotreating units would be necessary.

Still, important questions remain as to how the liquefaction and refining of coal liquids will interface, and additional research is needed to optimize this relationship.

In most liquefaction processes, a substantial degree of product slate adjustment can be achieved within the liquefaction plant itself by changes in the process variables. The relationship between cost of these changes and the cost of downstream refining must be considered. The most economical combination may require product slate adjustment in the main process, followed by appropriate downstream units for product upgrading to market specifications (12). For example, MacArthur et al (13) evaluated the merits of operating the H-Coal process in the mode of extinction recycle of 650°F+ vacuum gas oil, compared to typical H-Coal operating conditions. They concluded that

this operating mode improved the selectivity to liquid product and reduced commercial plant investment (including upgrading) by 10%, and the cost of producing coal liquids by 6%, compared to typical operation.

In addition to boiling range, another factor that has a large effect on the cost of refining coal-liquids is their hydrogen content. Because the finished fuels require a certain hydrogen content, it either must be added during the liquefaction process or during refining. Downstream hydrotreating makes efficient use of hydrogen, because it produces very little by-product light gas. Therefore, it may be cost effective to have a relatively hydrogen-poor liquefaction product (as that from the ITSL process shown in Table I), even though this adds to the downstream cost. Also, cheaper sources of hydrogen would significantly reduce costs. Furthermore, if the liquefaction and refining facilities were integrated, they could share the same hydrogen plant and additional costs could be saved.

The difficulty and, therefore, the cost of hydrotreating a coal-derived liquid increases rapidly with its boiling range, particularly if the endpoint is increased above 700°F. This is because of the high concentration of condensed aromatic and polar compounds in the high-boiling fractions which tend to cause rapid deactivation of the catalyst by coke deposition. Therefore, if at all possible, the high boiling fraction should be removed from the 700°F-oil before hydrotreating. Usually, the higher boiling oil can be used to advantage as recycle solvent in the liquefaction process. Clearly, sharp separation between the net liquid product and the heavy oil to be recycled is desirable. None of the oils shown in Table I contain large amounts of 700°F+, but even the amounts present have a very large deleterious effect. When this material is removed by distillation, the oils become much easier to upgrade.

Coal liquids boiling in the 700-900°F range are relatively hard to upgrade. However, it is technically feasible to hydrotreat coal oils in this boiling range to acceptable products. Almost certainly, the cost will be high, and more research is needed to optimize their upgrading. Clearly, from the viewpoint of the refiner, it is desirable to have them consumed as recycle solvent in the liquefaction process. Also, most of the biologically hazardous material is reported to be in the 700°F+ oil (2), and environmental problems in refining can be minimized if these materials are recycled to extinction at the upstream facility.

Any coal oils boiling above 900°F would be exceedingly hard to upgrade using conventional petroleum technology. New technology would be required to handle these materials.

ACKNOWLEDGMENT

This work was funded by the US Department of Energy under DOE Contract DE-AC22-76ET10532. The feedstocks were provided by Pittsburg and Midway Coal Mining Company; Hydrocarbon Research, Inc.; Exxon Research and Engineering; and Lummus Crest, Inc. The analytical work was performed by the Research Services Department of Chevron Research Company.

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2	FE-2315-45	SRC-I	November 1979
3	DOE/ET/10532-T10	SRC-II (Reissued)	November 1982
4	FE-2315-50	Paraho Shale Oil	June 1980
5	DOE/ET/10532-T3	H-Coal	September 1981
6	DOE/ET/10532-T5	SRC-II	April 1982
7	DOE/ET/10532-T11	H-Coal, EDS	January 1983
8	DOE/ET/10532-T17	H-Coal	September 1983
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TABLE I
 COAL - DERIVED PILOT PLANT FEEDS; COMPARISON OF PROPERTIES

Liquefaction Process	Whole Liquid (as Received)				Redistilled		ARABIAN LIGHT CRUDE	
	ITSL Illinois No. 6	H-Coal Illinois No. 6	H-Coal Wyodak No. 6	SRC-II Pitts-burgh Seam	EDS Texas Lignite	H-Coal Illinois No. 6		H-Coal Wyodak No. 6
Gravity, deg API	17.6	25.8	35.1	18.6	29.0	28.1	33.4	33.4
Sulfur, ppm	700	2000	410	2900	1180	1400	250	17000
Nitrogen, ppm	730	4600	1700	8500	3000	3300	1500	1000
Oxygen, ppm	1800	18000	8500	37900	13200	13600	6700	1000
Hydrogen, Wt%	10.68	11.29	12.74	10.46	11.25	11.44	12.97	13.10
Carbon, Wt%	88.99	86.25	86.20	84.61	86.41	86.13	86.18	85.77
Hot Pentane Insolubles, ppm	290	3500	680	469	1300	54	< 10	264
Remsbottom Carbon, Wt%	0.30	0.29	0.23	0.70	0.57	0.30	0.15	0.18
TBP Distillation, deg F @ St/ 5	97/214	56/177	53/156	56/189	53/164	56/170	52/165	47/142
10/30	314/471	213/333	173/261	241/379	203/317	200/310	178/269	171/296
50	560	404	354	424	370	380	356	342
70/90	609/676	476/588	429/535	473/562	452/662	440/508	424/509	404/512
95/99	703/763	654/765	602/785	642/820	799/950	538/589	542/603	547/627
Boiling Range, LV%	18	49	60	37	57	57	63	31
St - 400 deg F	76	48	38	60	35	43	37	53
400 - 700 deg F	6	3	2	3	8	0	0	1
700 deg F +								16

* Overhead, LV% of As-received Oil : 87
 Illinois H-Coal 96
 Wyodak H-Coal 87
 EDS 87

TABLE II

HYDROTREATING PILOT PLANT TESTS FOR COAL-DERIVED OILS

750 deg F Catalyst Temperature; Fresh ICR 106 Catalyst

Liquid Hourly Space Velocity	0.5	1.0	1.5	1.5
Hydrogen Pressure, p.s.i.a. (approximate)	2300	2300	2300	1800
<hr/>				
Re-distilled Illinois H-Coal				
Hydrogen consumption, SCF/BBL		2000	1950	
Product nitrogen, ppm		< 0.3	< 0.3	
Product aromatics, LV%		2	5	
Re-distilled Lignite EDS				
Hydrogen consumption, SCF/BBL			1600	1500
Product nitrogen, ppm			< 0.3	< 0.3
Product aromatics, LV%			6	10
Wyodak H-Coal				
Hydrogen consumption, SCF/BBL		1225	950	
Product nitrogen, ppm		< 0.3	< 0.3	
Product aromatics, LV%		3	13	
Illinois ITSL				
Hydrogen consumption, SCF/BBL	*	*	950	600
Product nitrogen, ppm			0.4	6
Product aromatics, LV%			38	58
Illinois H-Coal				
Hydrogen consumption, SCF/BBL	2150	1600	1275	825
Product nitrogen, ppm	< 0.3	0.3	10	50
Product aromatics, LV%	2	20	35	45
SRC - II				
Hydrogen consumption, SCF/BBL	3100	2500	2000	1725
Product nitrogen, ppm	< 0.3	0.4	20	150
Product aromatics, LV%	4	20	40	47
Lignite EDS				
Hydrogen consumption, SCF/BBL	1550		825	725
Product nitrogen, ppm	< 0.3		170	350
Product aromatics, LV%	16		38	40

*

The Illinois ITSL was tested at lower temperature.
The results:

L H S V	0.5	1.0
Temperature, deg F	710	730
H ₂ Consumption, SCF/BBL	1600	1400
Product nitrogen, ppm	< 0.2	< 0.2
Product aromatics, ppm	10	26

TABLE III

SUMMARY OF YIELDS AND REFINING COSTS FOR COAL-DERIVED OILS

F e e d		Yield of Desired Products, Liquid Volume Percent			(1) Total Investment, Millions of Dollars	(2) Refining Cost, \$/BBL of Desired Products
		motor gasoline	kerojet/ diesel	heating oil		
SRC - II	as received	21	66	-	1160	23.5
	as received	92	-	-	1030	20.5
	as received	25	-	63	870	17.5
Illinois H-Coal	as received	18	73	-	960	19.5
	re-distilled	20	72	-	850	17
	as received	96	-	-	950	18.5
	as received	20	-	75	660	13.5
Wyodak H-Coal	as received	28	65	-	750	14
	re-distilled	30	64	-	720	14
	as received	96	-	-	840	16
	as received	23	-	72	560	10.5
Lignite EDS	re-distilled	24	67	-	740	15
	as received	97	-	-	960	19.5
	re-distilled	88	-	-	820	15.5
	re-distilled	23	-	66	710	14.5

- (1) On-plot + off-plot + initial catalyst for capacity to produce 50,000 barrels per calendar day of desired products; first quarter, 1984. Excludes all costs for coal resources, mining, handling, liquefaction, and transportation.
- (2) Calculated rigorously by discounted cash flow analysis using 15% after-tax constant dollar rate of return, 6% background inflation rate, 100% equity financing, 48% income tax, 10% investment tax credit, depreciation according to 1982 Tax Equity and Fiscal Responsibility Act, 5-year tax life, 20-year project life.

FIGURE 1
DISTILLATIONS OF
ARABIAN CRUDES AND COAL-DERIVED OILS

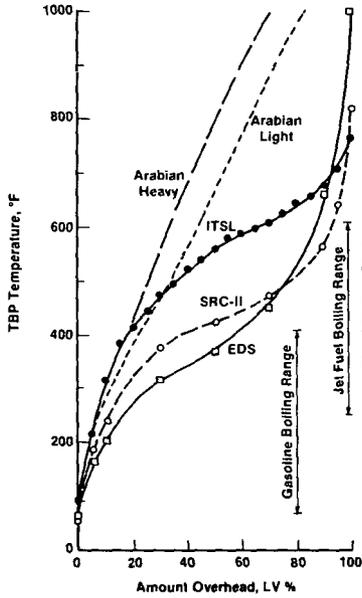


FIGURE 2
REFINING OF COAL SYNCRUDE TO
TRANSPORTATION FUELS

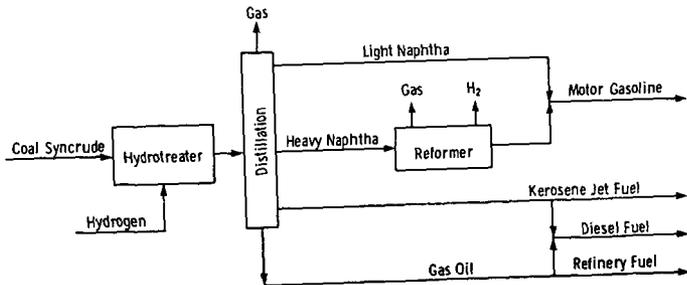


FIGURE 3
REFINING OF COAL
SYNCRUDE TO GASOLINE

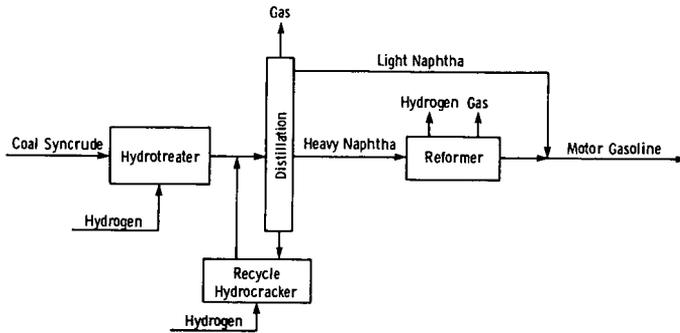
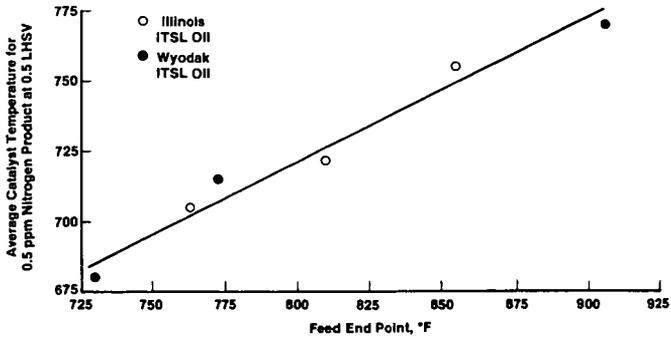


FIGURE 4
DOE CONTRACT DE-AC22-76ET10532
EFFECT OF FEED END POINT ON CATALYST
TEMPERATURE FOR HYDRODENITROGENATION OF
ITSL OILS WITH FRESH ICR 106 CATALYST
H₂ Partial Pressure = 2300 psia
Liquid Hourly Space Velocity = 0.5



DIRECT COAL LIQUEFACTION: BRIDGING THE GAP BETWEEN R&D
AND COMMERCIAL FEASIBILITY

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INTRODUCTION

The more recent development of direct coal liquefaction processes for rapid commercial readiness started in 1975 and culminated in 1982. Four processes, SRC I and II, H-Coal and Exxon Donor Solvent (EDS) were at the point where they were considered serious contenders for commercialization (1,2,3).

Based principally on the experience gained in large pilot plants for each of the above processes, it could be stated that commercial-scale direct coal liquefaction facilities could be designed and constructed using available technology to give predictable yields and acceptable mechanical performance.

All the processes which were considered technologically ready for commercialization as well as those recently developed in process development units (PDU), i.e., Two-stage Liquefaction, were based on research done at laboratories of companies involved in petroleum processing. Their experience in petroleum residues processing, which turned out to be somewhat similar to direct coal liquefaction processing, gave them a leading hedge over other DOE supported laboratories involved in fundamental and applied research in direct coal liquefaction.

In this period of major effort for ERDA/DOE (1975-82) we learned that the development of this industrial technology requires meaningful cooperation among many scientific disciplines, including several branches of chemistry, physics, engineering, economics and others. It requires superior management to achieve a proper balance among the several branches involved, as priority shifts from one discipline to the other according to the progression of problems encountered. This is particularly true for direct coal liquefaction technology that involves complex operations, and deals with, what is now believed, a mixture of mostly reactive and partly refractory materials.

During the last three years, with the drastic curtailment of the DOE budget, and the shift towards novel research approaches, most of the recent applied research efforts were focused on a single aspect of coal liquefaction, namely obtaining high coal conversion, and neglecting other important coal processing components, i.e., the upgradability of the converted coal extracts produced from high conversion. An upgradability test would reveal whether the conditions used in converting the coal were too drastic, producing "refractory" compounds which would be difficult and expensive to downstream processing. This example and other neglected requirements for useful coal processing revealed a widening gap between fundamental and applied research direction on one hand, and process technological advances directed toward possible scaleup, on the other. This technological gap needs to be bridged and more meaningful coordination between R and D ought to be augmented. It is for this purpose that this paper is addressed to those researchers who are interested in pursuing the scaleup of research discoveries by pointing out the technological needs for their development into feasible process scaleup configurations and the production of marketable fuels. Also the paper summarizes some recent trends in direct coal liquefaction technology, which either have achieved or have the potential to achieve developmental stages, to serve as possible guideline for future research.

BACKGROUND AND RECENT DEVELOPMENT

Earlier approaches to direct coal liquefaction have employed high severity operating conditions of pressure, temperature and coal/solvent slurry contact time, to achieve in one reactor the highest coal conversion and distillate yield possible. Several disadvantages are associated with this processing mode, namely: 1) the high hydrocarbon gas yield which causes high hydrogen consumption, 2) the production of lower quality solvent containing low boiling distillates, 3) the "regressive" formation of high boiling distillates and non-distillables which are "refractory to hydrogenation" and are the major cause of hydrotreating catalyst deactivation, 4) the extreme difficulty in controlling the highly exothermic reaction of molecular hydrogen with aromatics, particularly in large scale units, and 5) the production of lower quality distillate fuel products which require more severe hydrotreatments to meet transportation fuel specifications.

The accepted main mechanism for high severity conversion of coal is the homolytic thermal cleavage of bonds to yield free radicals, which are capped by hydrogen from the donor solvent or hydroaromatic structures in coals.

A more recent approach uses low severity operation in separated stages in order to optimize the coal dissolution step and coal extract upgrading step. The result is to substantially reduce, and in some cases eliminate, the disadvantages created by high severity processing.

Integrated staged operations in continuous units at Lummus, Wilsonville, Kerr-McGee and HRI have produced enhanced yields of high quality distillate product and recycle donor solvent, both with much reduced heteroatom content and lower hydrogen consumption compared to high severity single-stage processing (4).

Recent work on integrated staged coal liquefaction processing and other DOE supported projects, as well as development of new analytical techniques, have provided substantial amounts of new information. The result has been to change substantially our approach to coal liquefaction techniques and to inspire new thoughts in unraveling the complex mechanism of direct coal liquefaction at low severity operations. Important new information includes:

Low severity processing forms mostly reactive low molecular-weight fragments. Conversely, single stage thermal and thermal/catalytic processing produce high-molecular weight products thought to be actually condensation products of such smaller fragments and consequently, less reactive (5).

Thermally produced coal extracts contain a high level of heteroatom compounds and are "refractory" to catalytic hydrogenation (6). Conversely, low severity produced extracts are low in heteroatoms and more easily hydrogenatable, consistently yielding excellent equilibrium donor solvent, as proved in all Integrated Two Stage Liquefaction (ITSL) operation (7).

No high viscosity gel region is apparent over the 280-350°C temperature range for a slurry of bituminous coal and ITSL solvent, as was the case for slurries prepared with the same coal and other types of solvent (8).

Proton NMR analysis, modified to provide data on ITSL distillate and non-distillate fractions, serves to create a kinetic model for coal extract hydroprocessing, thus enabling us to distinguish catalytic hydrogenation and cracking reactions, and to predict the solvent donor capability as well as the yield structure of the upgraded products (9).

A mixture of condensed aromatics, hydroaromatics, paraffins and their respective heteroatom derivatives is produced during coal liquefaction. This mixture tends to be unstable because of the incompatibility between polar heteroatom compounds and hydrocarbons, as well as between condensed aromatics and paraffins. Condensed hydroaromatics, having closer affinity for both aromatics and paraffins, tends to keep them in solution, thus contributing to the stability of the coal extract. Low severity coal extraction yields larger quantity of hydroaromatics and smaller amount of high heteroatom, condensed aromatics and paraffins (9)

Best catalysts tested are those modified to suppress the hydrocracking activity and enhance hydrogenation functionality (7).

Coal derived transportation fuels possess inherent high premium quality which due mostly to their hydroaromatic (naphthenic) nature. Coal-derived naphthas contain large quantities of highly alkylated cyclohexanes which, by reforming, convert to the corresponding benzenes and in the process, recover a large portion of the hydrogen to make the overall coal liquefaction approach economically more attractive. Alkylated benzenes are the major contributors to the high octane gasoline thus formed. Coal derived middle distillate is constituted mostly of di- and tri-hydroaromatics and corresponding aromatics. Refining must convert the aromatics to less than ten percent level to meet marketable jet and diesel fuel specifications of smoke point and cetane number, respectively (10).

Phenols inhibit catalytic denitrogenation of coal derived liquids (11). Nitrogen compounds inhibit catalytic hydrogenation of aromatics (12).

Recycle solvent produced at high severity (SRC-I) and modified by removing part of the heteroatom compounds, produces significantly higher oil yield and coal conversion compared to the data obtained with the unmodified solvent (13).

SIGNIFICANCE OF RECENT DEVELOPMENT

Processing coals at low-severity operations has the potential for simplifying the process scheme, drastically reducing reaction severity and instability of the reaction intermediate products, and yielding superior quality fuel products.

Novel research approaches will have to compete against the superior achievements obtained at low-severity processing, rather than citing small improvements over high-severity processing results.

Other significant conclusions derived from low-severity liquefaction are:

A mechanism of the initial coal extraction different than that for the high severity operation must be invoked for the low severity conversion in which coal and donor solvent first form an "adduct," possibly by interaction of both hydrogen and covalent bonds. Bond cleavage of the adduct is accomplished by weakening the coal aromatic structure through hydrogen transfer from the donor solvent to the coal. This overall hydroaromatic structure is more easily cracked thermally.

The apparent non-intervention of the hydrogen gas in the donor solvent/coal reaction, in spite of the imposed high hydrogen partial pressure, would indicate that the donatable hydrogen present in the solvent is transferred much faster to the coal than the hydrogen gas which has to transfer first to

the solvent and finally, to the coal. Also, donor solvent-coal reaction is seemingly faster than the occurrence of most repolymerization reactions known as "regressive" reactions. In the absence of a reacting gas phase the SCT reactor flowdynamics would be reduced to relatively simple liquid/solid two phase reaction, anticipating better correlation between data produced in bench- and scale-up units.

Removal of heteroatoms from freshly formed preasphaltenes might be sufficient to convert them to toluene solubles and ultimately to yield mostly hydroaromatics.

The low severity coal extraction is apparently thermally neutral in that the exothermic hydrogenation of condensed aromatics is equalized by the endothermic dehydrogenation of the hydroaromatics, the major constituents of the donor solvent. Thus, low severity extraction is inherently much more controllable than the exothermal hydrogen-gas/solvent/coal high severity reaction, an extremely important factor in scale-up operations.

GENERAL THOUGHTS AND RECOMMENDATIONS

First of all we need to recognize that future coal liquefaction commercial efforts will be market-driven instead of technology-driven. In some industries like computers, a technical breakthrough creates a new market. For coal liquefaction, and for synfuels in general, the market will point the direction and technology will clear the path.

With these thoughts in mind, one needs to acknowledge that the cyclic nature of coal derived products, eventually containing some of the heteroatom impurities will require new standard specifications for their safe use. Consequently, to meet today's fuel specifications and avoid possible unknown problem in the future, one must first practically remove most of the heteroatoms and all of the mineral matter from coal liquids. Obviously it would be advantageous to remove a large portion of the mineral from the organic matters prior to introducing coal into the slurry vessel. Also advantageous would be to either remove the heteroatoms in the early stage of coal extraction and/or to weaken the carbon-heteroatom bonds for ease of heteroatom removal in subsequent stages. Experimental results at Suntech (11) advises to remove first the more abundant oxygen, which seems to tie up the nitrogen compounds via hydrogen bonding, and thus making easier the subsequent nitrogen removal.

Complementary fundamental studies on C-O and C-N bond scission should be emphasized over the current C-C bond cracking effort.

Most of the sulfur is converted to hydrogen sulfide during liquefaction and upgrading, and the H_2S must be kept in the system as catalyst itself and as "activator" of transition metal catalysts.

Preservation of highly reactive, small fragments in the coal extract is of utmost importance in producing an excellent donor solvent and high quality distillate fuel products. For this purpose, the fragments should be withdrawn from the extraction reactor as soon as they are formed. The unconverted coal can be further converted by recycling it with the preasphaltenes as part of the recycle solvent. This approach appears to be especially successful in processing low reactivity coals such as Wyodak subbituminous coal (7) and supports the claim (14) that conversion is not coal limited but process limited.

Better preservation of the reactive small fragments can be achieved by increasing the donatable hydrogen level and decreasing the heteroatom content of the recycle solvent. It is important for the donatable hydrogen to match the hydrogen acceptability of the coal as both conditions become more reactive with increasing temperature. Consequently, it is advisable to allow for a thermal soaking treatment, i.e., at 250-350°C temperature range for 10-30 minutes, prior to a very short contact time (SCT) action of rapid heating (two minutes or less) to the 450°C exit temperature. It is evident that all the above activities are interdependent and the improvements maximized in an integrated recycle process.

It is extremely difficult to capture in research bench scale units the essence of the results produced in the integrated recycle process, because most of the key benefits, i.e., coal conversion and enhanced donor solvent quality, are obtained only after several cycles of the integrated staged operations. Bench scale researchers could avoid the long and tedious recycle operations by applying the aforementioned kinetic model for coal extract hydroprocessing (9) and using proto-NMR data of the coal extract to predict solvent donor capability and yield structure of the upgraded products.

The recommendations made will also preserve the highly valuable cyclic characteristics of the final fuel products, minimizing the formation of paraffins. Conversion of hydroaromatics to either paraffins or to aromatics, if desirable to meet fuel specifications, is achieved under easy and controlled operations.

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A Perspective on the Future of Synthetic Fuels

by

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In a letter from Office of Management and Budget Director James Miller to Members of Congress in the final days of the 99th Congress, the Reagan Administration stated that "continued funding of the Synthetic Fuels Corporation serves no useful purpose". The Congress reacted by eliminating funding for the SFC. A four month phase down period is coming to an end as we meet here today. Of course, only time will tell whether abolition of the SFC was a wise and prudent move or a short-sighted act of folly. What should be clear, however, is that development of synthetic fuels technologies in the U.S. and worldwide will continue for reasons that are rooted in the necessity of industries and governments to be assured of an adequate supply of energy at reasonable prices amid a glut of uncertain signals over the nature of our energy future.

This paper looks at the American experience with synthetic fuels development in the wake of the energy crises of the 1970s, assesses the progress that has occurred, and analyzes the political and economic factors contributing to the abolition of the U.S. Synthetic Fuels Corporation.

Looking ahead, the paper presents the author's views on the future of advanced fossil fuel technologies in the utility, industrial, and transportation sectors in the absence of the federal synthetic fuels incentives of the early 1980's.

The paper concludes by discussing the major uncertainties and institutional complexities that must be considered in private sector decisions with respect to synfuels investments and that will play a role in shaping energy policy in future administrations.